

Gasoline Removal During Dynamic Underground Stripping: Mass Balance Calculations and Issues Chemical Fractionation

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Gasoline Removal During Dynamic Underground Stripping: Mass Balance Calculations and Issues Chemical Fractionation

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During the first pass, about 1700 gallons of gasoline were removed. Most (74%) of the gasoline was removed from the vapor stream by the carbon trailer. Another 17% appears to have been condensed (cyclone separated) from the vapor stream, and the remainder was recovered dissolved in groundwater. During the second pass, 4900 gallons were removed. Approximately 77% was recovered as vapor and burned in the IC engines; 21% was condensed (cyclone separated) from the vapor stream and the remainder was recovered in groundwater. The ARV phase removed 1080 gallons; 84% was burned in the IC engines and 10% was condensed. Total removal was 7680 gallons, plus or minus estimated error of 900 gallons derived from: analytical uncertainties, flow rate fluctuations, and conversion from mass to liquid volume.

Chemical measurements from the vapor, liquid, and condensate streams indicate that most of the gasoline was removed from the vapor and condensate streams. The condensate appears to have been mainly composed of droplets that were removed from the vapor stream by the cyclone separator; the vapor equilibrated at the temperature of the groundwater before reaching the condenser. This is probably due to contact with the cold air in the pipes leading to the air-lift pumps, and hot water pumped back to the surface, as well as contact with cooler air drawn in at the top of the screened zone.

Although some fractionation/distillation appears to have occurred during the removal process, most of the gasoline appears to have been removed by a mechanism dominated by nearly complete volatilization of localized volumes of gasoline and water, resulting in fairly minor and often-reversed changes in overall chemistry of extracted gasoline with time. Only during the ARV phase did significant changes in chemistry occur, with the majority of the volatile BTEX and light hydrocarbon species disappearing from the effluent.

Introduction

Measuring the total gasoline removed by Dynamic Underground Stripping proved to be difficult because of the dramatically different rates and makeup of the effluent compared to more conventional extraction methods. During the first pass, two incorrect assumptions were made. First, we assumed that an accurate assessment of the amount of gasoline in the vapor stream could be made from the amount of gasoline removed (and recycled) by the automated carbon system. Flow in the vapor stream proved to be much larger than anticipated, enhancing the error from this assumption. Second, we assumed that the amount of gasoline in the water system would be easily measured by the concentration at the port SEPI and the amount of raw gasoline separated in the oil-water separators (Figure 1). The amount of gasoline in the condensate stream (steam and gasoline condensed from the vapor stream) was not measured separately. These factors led to some uncertainty in the amount of gasoline recovered from the first pass; during the second pass, the monitoring strategy and sampling locations were changed to adequately sample both the vapor and the liquid.

Mass balance calculations for Dynamic Underground Stripping were based on information from the following streams:

- Vapor: The dried gas phase stream after the heat exchanger and cyclone separator/demister.
- Condensate: The liquid recovered from the heat exchanger/demister system (accurately measured during the second pass and ARV phase only).
- Groundwater: The liquid pumped out of the wells, with incidental water from the treatment system such as condensed water from the heat exchanger.

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Effluent Treatment System, Dynamic Underground Stripping

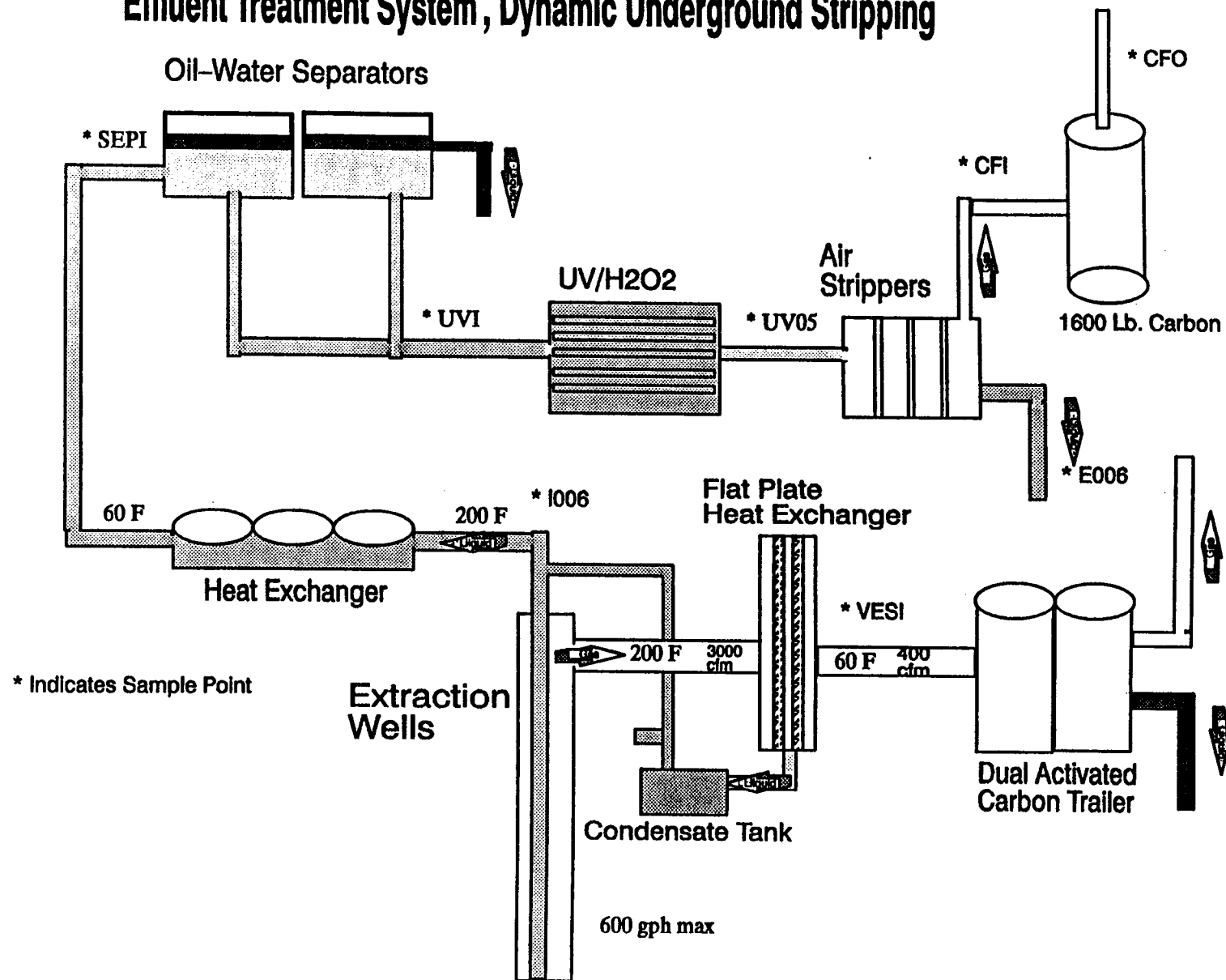
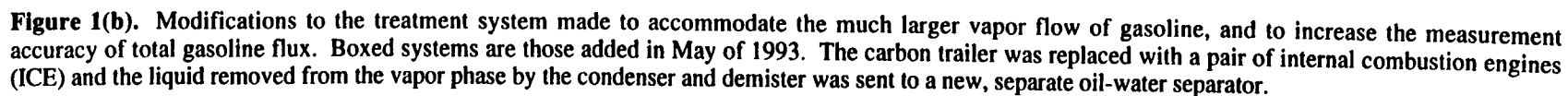


Figure 1(a). Original treatment system used during the first pass of Dynamic Underground Stripping (February 1993) with notations for the significant sample ports and measurement points. Vapor comes up the well annulus around the water extraction pipes. (See Siegel and Sorensen, *this report*, for treatment system description.)

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Each of these streams requires a separate calculational strategy. Second-pass modifications ensured that the streams were separate and could be measured independently.

We made measurements of the gasoline content of liquid and vapor in terms of the typical TPH (Total Petroleum Hydrocarbons), which nominally includes molecules with 6 to 12 carbon atoms, as well as a more inclusive second-pass category designated HC (Hydrocarbons), which includes all peaks discerned on the gas chromatograph (nominally from 2 to 12 hydrocarbons). All mass balance calculations in this article use the HC values when available. These are assumed to be equivalent to an actual volume of gasoline, such as those measured from the oil-water separators. This assumption may be in error but no direct tests have been conducted to determine the volume of a given mass of gasoline recovered in this experiment.

When some of the charts used in this paper were prepared, the only mg/l values were for TPH, so the corresponding HC values were calculated from the ratio of HC/TPH vol/vol values. Minor discrepancies from the data of Jovanovich (*this report*) may occur due to this. Gasoline density of 100 g/mole liquid (737 g/L) was used in these calculations (Lyman et al., 1991). This value was only used to calculate the volume of liquid represented by a mass of gasoline determined from vapor.

Time Indexing - Second Pass

Time indexing can have a significant effect on the calculation of mass flux due to the highly varying rate of gasoline removal. In the first pass, this effect was not apparent due to other problems in the analyses. In the ARV phase, the zero time was chosen so as to minimize the effects. Second pass data are the most strongly affected by this, and also represent the largest volume of removed gasoline.

The zero time for the second pass was 8:00 am Sunday, May 23. Days are calculated as fractions, so day 1.00 was Monday at 8:00. When data was averaged over 24 hr in the ICE IN spreadsheet, the data was indexed to the end of the period. Therefore, the calendar date for the averaged data is one day ahead of the calendar date for any chemical data or other point measurements. The first day of averaged operational data is dated May 25 and indexes to chemical data from May 24. Although this results in a slight offset in the center point of the average and point measurements (8 PM for the averaged operational data such as flow rate, but typically about 10 am for the two averaged vapor samples), the offset appears to be less trouble than trying to change to another time indexing scheme for the second pass (all point measurements are collected at different times anyway). This is shown graphically in Figure 2 for the flow and chemistry data recorded for June 30 (second pass).

Vapor System

The gas phase recovered after the heat exchanger and demister contains most of the gasoline extracted during Dynamic Underground Stripping, and it is also the most difficult stream to measure due to variability and the difficulty of making gas-phase measurements. The vapor-stream treatment was changed between the first and second passes; during the first pass gasoline from the vapor system was accumulated on to activated carbon, and during the second pass and ARV phase, it was burned in an internal combustion engine.

The first component of the vapor analysis is the measurement of the total gas flow into the carbon trailer or IC engines. During the first pass, the carbon trailer's fixed displacement pump displaced 370 scfm (400 acfm). This fixed value corresponded with the measurement from the Merriam gauge. The Merriam gauge has been determined to be the most accurate means to determine flow during the second pass, as it matched the first pass value well and appears to be subject to the fewest uncertainties (see discussion in Siegel, *this report*). The differential pressure read on this gauge is converted to flow in actual cubic feet per minute using the manufacturer's calibration (observed pressure differential in inches of water times 53.5). It is then corrected to standard pressure using the observed vacuum at the IC engine. In the ICE INPUT spreadsheet, it was also corrected to an assumed temperature of 58°F. This may introduce a minor error (see Figure 3) as the temperature in the gas stream after the heat exchanger was observed to fluctuate diurnally; however, as is seen in Figure 3, the error would be small.

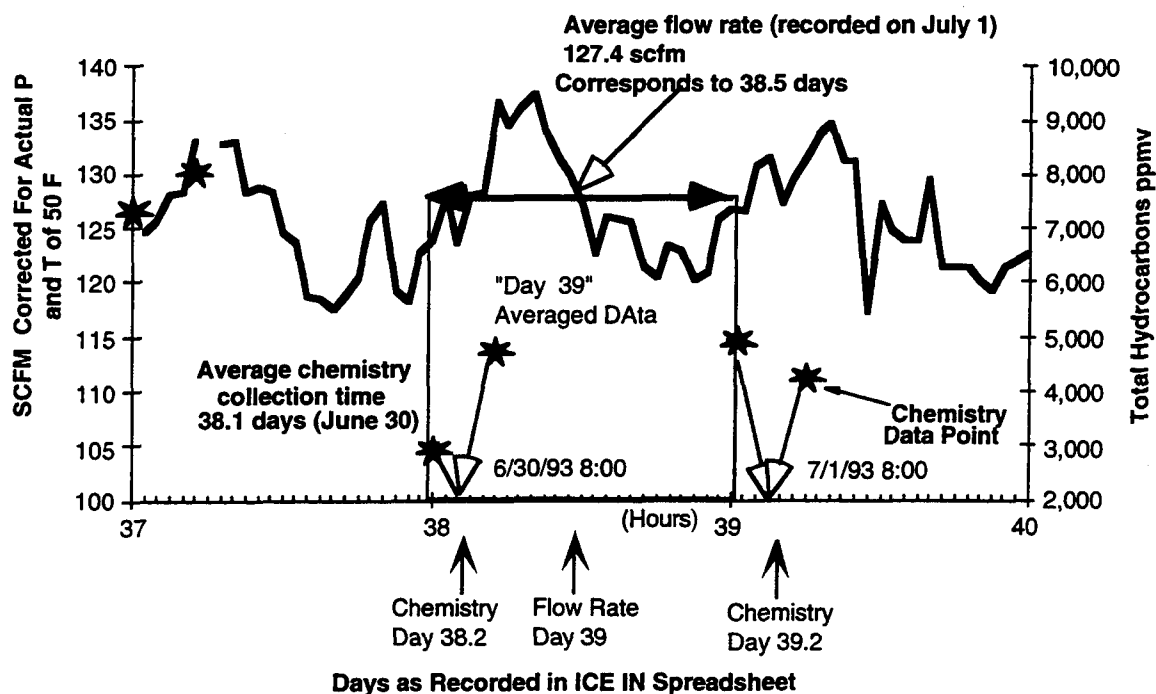


Figure 2. Time indexing during the second pass. Examples are shown for the time variability of the flow rate (solid trace) and chemistry measurements (stars), compared to the date and day-count.

During the first pass, the volume of gasoline removed from the vapor stream was measured directly in liquid volume from the accumulating barrels outside the carbon trailer, which were measured every hour. This value was corrected as needed when the barrels were transferred into a large storage tank. The hourly measurements proved to be the most accurate means of determining the rate since a large number of measurements were made each day. This value for the total does not include any gasoline that passed through the carbon canisters without being adsorbed. This amount is assumed to be negligible, but carbon trailer malfunctions could have passed unadsorbed gasoline through the system after a canister saturated. During the first pass, a total of 1264 gallons of gasoline were accumulated from these barrels, or 74% of the total volume removed in the first pass.

No total hydrocarbon concentration measurements were taken on the gas stream during this phase, as it was assumed that not much of the gasoline would pass the condenser, and that the carbon trailer would function as intended and recover 100% of the gasoline. As such we have no direct measurements to compare to the second pass gas measurements. However, knowing the flow rate and the total recovered gasoline, we can calculate the equivalent gas concentrations (ppm HC) to the second-pass measurements. These are shown in Figure 4 and listed in Table 1. The calculated concentration ranged up to 3500 ppmv directly after first breakthrough (at about 12 days) and averaged nearly 2000 ppmv during the later portion of the second pass. BTEX measurements were taken at the VESI port (before entry into the carbon trailer). Although BTEX ratio to TPH is known to vary, the BTEX measurements are also included in Figure 4 for comparison. The average fraction of BTEX in all the data used for Figure 4 is 57% (Jovanovich, *this report*), an extremely high value. Note that the trends in the data match well at this value (the scales have been adjusted to show this conjunction).

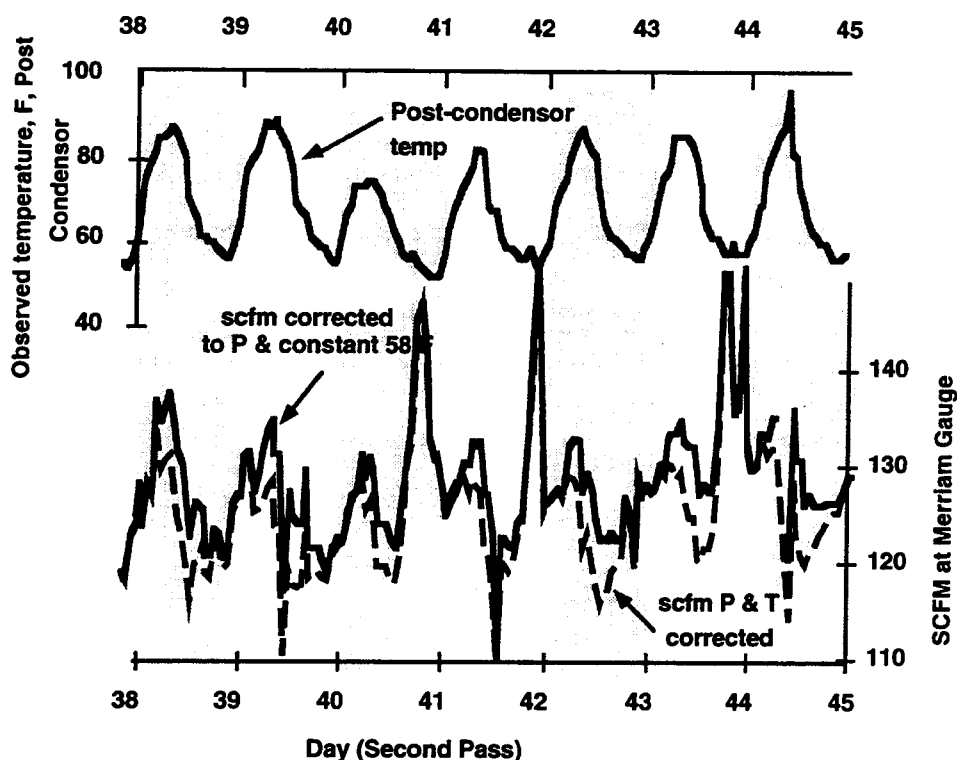


Figure 3. Temperature and flow data from ICE INPUT spreadsheet (W. Siegel) showing the minor effect of temperature correction on the data during the second pass, and the large observed temperature changes in the vapor flow. Top: temperature measured in the dried vapor stream after the flat plate heat exchanger. Bottom, solid; the volumetric flow rate measured as "actual" cubic feet per minute of gas, corrected for observed pressure and a fixed temperature of 58°F. Bottom, dashed; fully-temperature corrected flow rates using post-condenser temperature (top trace).

The 2000-ppmv value (total hydrocarbons), which appears to be the limiting value in all but one case (see below), might be interpreted to represent saturation of air with gasoline under these pressure and temperature conditions; in particular during the last several days of the first pass when recovery rates jumped dramatically, no increase in the carbon trailer recovery was noted. Two of the days in the first pass show strongly anomalous data for percent BTEX and total hydrocarbon. It is assumed that the points on days 11 and 35 are either in error, or that the carbon trailer system was allowing a significant amount of gasoline to pass the carbon canisters, as discussed previously. These days correspond to unusual events in the process; day 11 was the beginning of steam break through to the extraction wells, and day 35 was the close of the first pass. At that time (discussed below), water chemistry showed extremely high TPH values and anomalous chemical ratios.

The 2000-ppmv value is far lower than would be expected for gasoline saturation and is much lower than values noted routinely in the second pass. Therefore, it may represent an operational limit on the carbon trailer system; gasoline beyond the 2000-ppmv limit may have saturated the carbon canisters and been exhausted without treatment. The automated effluent monitoring systems on the trailer were not functioning properly, and one measurement of the effluent from the trailer (EOO6 VPR) is known to have exceeded the established limits on day 11 (Jovanovich, *this report*) which resulted in a notice of violation from the regional air quality control board. Few measurements of the effluent from the carbon canisters were taken at that time as we were not aware that the automated systems were not functioning

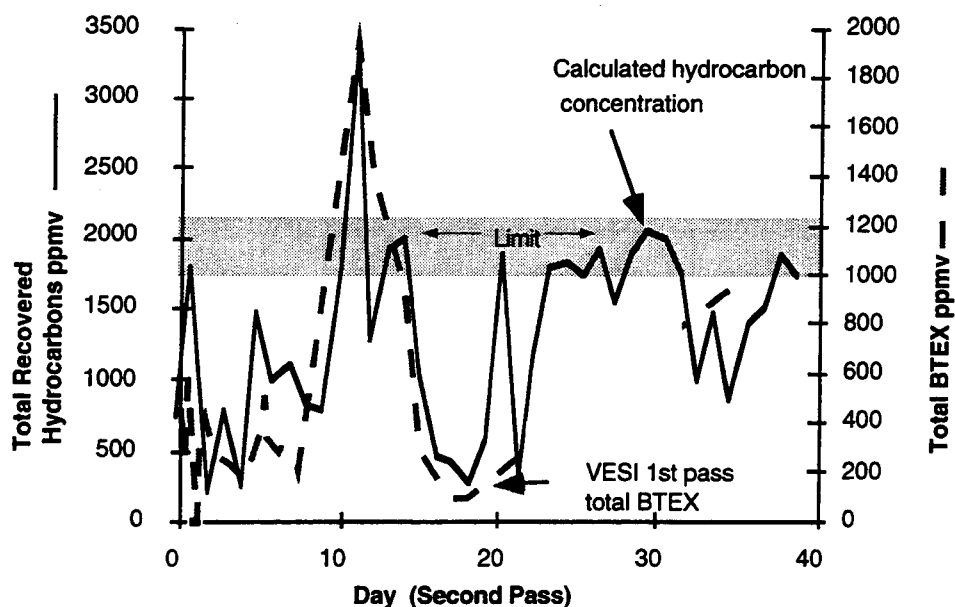


Figure 4. Calculated vapor concentrations (post-condenser) from the first pass. Note time offset: calculated total hydrocarbons data actually refer to average for previous 24 hr and should be moved back in time 1 day.

properly. Measurements on days 33 and 35 were also high (Jovanovich, *this report*). Gasoline smell was occasionally noted around the carbon trailer, which we now know should not occur if the carbon is absorbing all the gasoline. Although these arguments suggest some gasoline was escaping the system, no quantitative measure can be applied to this amount. Therefore, the vapor recovery rate is tabulated as only that recovered as liquid gasoline (1280 gallons). This effect is discussed further in the section on integrated vapor/condensate measurements (IOO6) below.

Table 1. Observed and calculated vapor composition, first pass.

Date	Days	Measured Benzene (ppmv)	Calculated HC (ppm)	Measured BTEX (ppmv)	BTEX (%)
2/5/93	2	60	1789	484	27%
2/6/93	3	18	203	353	173%
2/7/93	4	15	773	232	30%
2/8/93	5	36	244	170.1	70%
2/9/93	6	39	1464	409	28%
2/10/93	7	15	976	293	30%
2/14/93	11	307	1098	1940	177%
2/15/93	12	102	3375	1,389	41%
2/16/93	14	83	1260	946	75%
2/17/93	15	48	1911	291	15%
2/19/93	17	3	1016	93	9%
2/20/93	18	5	447	97	22%
3/8/93	35	35	975	967	99%

During the second pass, the average flow values reported in the ICE INPUT spreadsheet are derived from the Merriam flow gauge values corrected for actual pressure and temperature of 58°F. Vapor chemistry was measured at the port ICE-IN [Figure 1(b)] during the second pass. The chemistry data collected from that airstream must also be pressure corrected; however, most of the chemistry vapor samples were collected in Teflon plastic bags that automatically correct to ambient pressure and temperature. Other samples collected in steel spheres were corrected to standard pressure and temperature (Jovanovich, *this report*). All were then reported in mg/L. The total mass of gasoline burned by the IC engine in a 24-hr period is then:

Mass = volume total gas (liters) times concentration (mg/l)

The volume of gasoline assumes a density of 737 gr/L (Lyman et al., 1991).

A total of 3805 gallons of gasoline were burned in the second pass.

Error Analysis: Errors associated with this measurement are in the flow rate, concentration, and conversion factors. The first-pass accounting is assumed to be essentially free of error since the amount of gasoline was measured directly as condensed liquid. As discussed previously, there are other possible sources of error that cannot be quantified, and will not be included in this estimate. The only included error is in the liquid measurement. Without independent measurements, the second-pass flow rate must be assumed to be accurate to the readability of the gauge, better than 1%, when averaged over 24 readings per-day. Concentration measurements are subject to a multitude of errors, as yet unquantified but reasonably on the order of less than 10% (Jovanovich et al., *this report*). The large diurnal variation in concentration may be resolvable using the continuous monitoring data, (Barber, *this report*) and for now it appears reasonable to assume that the averaged chemistry data is reasonably well correlated with the averaged flow data (using the same time indexing, Figure 2). However, there could be a systematic error in the chemistry data. The conversion to liquid volume has perhaps a 5% error depending on initial concentration and weathering. Allowing for up to 10% systematic error in the chemistry makes all these uncertainties additive, and leads to an (assumed) error of $\pm 16\%$, or ± 600 gallons during the second pass and ± 150 gallons during the ARV phase.

Vapor Recovery:

First pass	1260 \pm 20 gallons
Second pass	3805 \pm 600 gallons.
ARV	909 \pm 150 gallons

Condensate

First Pass. Measurement of gasoline condensed from the vapor stream was very difficult in the first pass due to unexpected difficulty in sampling the condensate stream (no sample port existed in the original pump-and-treat design at this point, and we failed to add one for the first pass). All liquid removed from the vapor stream was transferred from the condensate tank several tens of gallons at a time, into the main-liquid water stream. Any condensed gasoline should have then been removed in the main oil-water separators. The relatively small amount observed there may have, in fact, been from this source, but no independent measurements could be made. We attempted to make measurements of the fraction of gasoline present in the condensate tank. When the tank was nearly full, a "core" sample was removed using a barrel sampler. This measurement always showed some free-product gasoline present, but the tank also never completely emptied. Figure 5 shows the percent of gasoline measured in the condensate tank, along with the amount of gasoline recovered in the oil-water separators.

For the purposes of the mass balance, calculation it is assumed that no other gasoline was condensed.

Second Pass and ARV. During the second pass direct and unequivocal measurements of gasoline in the condensate were made by transferring it to a dedicated oil-water separator [Figure 1(b)]. The system was re-plumbed so that all water accumulated from the vapor stream (condensed by the flat plate heat

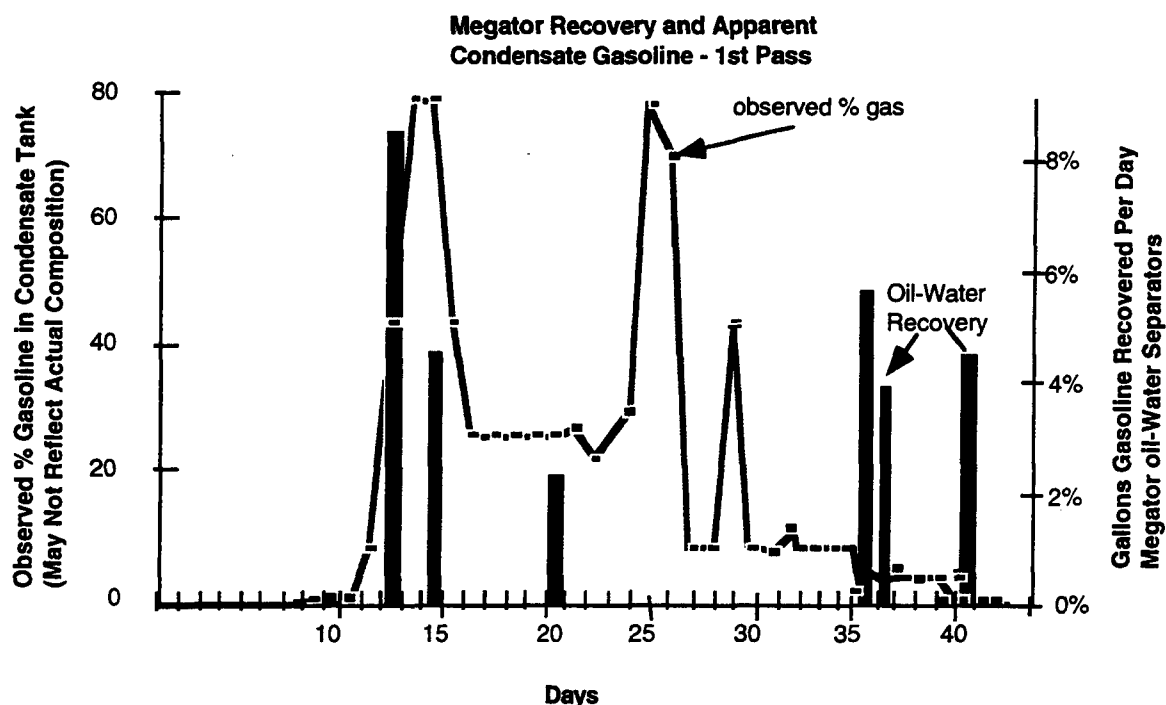


Figure 5. Solid trace: Percent gasoline observed in first-pass measurements of condensate. Bars: Observed pulses of gasoline product in the oil-water separators. Gasoline was not recorded until emptied, so actual accumulation occurred prior to or on date noted. The measurement of percent gasoline in the condensate was very difficult in the first pass, and should be regarded as having a very high error associated with it.

exchanger or droplets removed by the cyclone separator) was handled as a separate stream. The volume of condensed gasoline could then be measured directly from the liquid. Some water occasionally spilled into the gasoline collection side, of the separator, increasing the apparent amount of gasoline recovered, but this was checked in the large storage tank using an interface probe. The amount of water and gasoline in the storage tank was used to correct the amount of gasoline that had come out of the separator. (Some water was counted as gasoline in that initial transfer measurement.) Water spill-over in the separator occurred at least twice during the operation,. This resulted in two columns in the original ICE INPUT spreadsheet (W. Siegel), the first being the original measurement of transferred fluid from the oil-water separator, the second being that value minus the water content. Figure 6 shows the time variation of the (corrected) recovery of gasoline and water from the condensate system. Initial second-pass recovery was extremely high, apparently due to the presence of hot, free-product gasoline near the extraction wells. This behavior is similar to the large pulse of gasoline recovered early in the first pass.

The relatively low volumes of condensed gasoline relative to gasoline burned in the vapor phase are a result of the very high flow rates of inert gas in the system. This inert, noncondensable gas is presumably air pulled in from the formation and atmosphere, including air pulled in at the top of the screened zones above the heated area. This air (about 120 to 150 cubic feet per minute) could carry a large amount of gasoline to the IC engines. Condensate recovery could be enhanced by limiting the influx of inert gas, which would also raise the applied vacuum on the treatment area.

Error Analysis. We measured gasoline volumes directly during both passes, so no conversions are necessary. During the second pass, we measured the gasoline in the oil-water separator hourly to ± 2 gallon for each transfer, and the volume in the storage tank could be read using its internal gauge to approximately ± 25 gallons; these both support an error of no greater than ± 25 gallons. During the first pass, there is considerable error possible because the oil-water separators were not adjusted properly, and

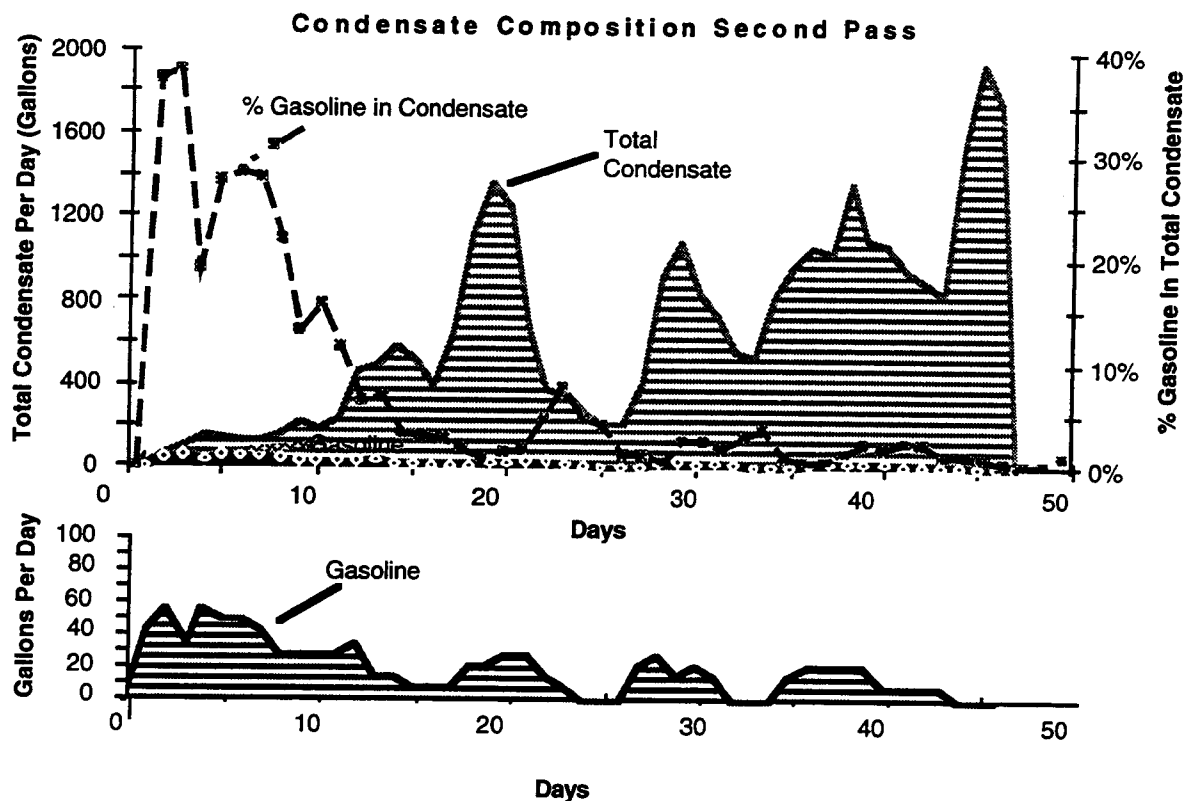


Figure 6. Second-pass condensation of water and gasoline from the vapor stream (expanded scale for gasoline below). The amount of gasoline recovered from condensed liquid varied from almost 40% to less than 1%.

some gasoline may have been carried into the UV machine. At the close of the first pass, the UV machine was opened for cleaning and found to contain some free product inside the treatment passages. Free product passing through the UV machine would have been removed by the air-stripping system (Siegel, *this report*). It is possible that as much as 100 gallons could have been missed in this manner if there was a continuous loss of this kind; more than that would have shown up as increased amounts in the UVI measurements or as increased loading of the 1600-lb carbon canister (Siegel and Sorenson, *this report*).

First pass: 260 + 100 gallons
 (approximately 17% of vapor stream)
 Second pass 1012 ± 25 gallons
 (approximately 21% of vapor stream)
 ARV 107 ± 5 gallons
 (approximately 10% of the vapor stream)

Combined Vapor-Condensate Sampling; Port IO06

In theory, the discrepancies and difficulties noted in the analysis of vapor and condensate streams could be eliminated by sampling the hot vapor stream before the condenser. Port IO06 (Figure 1) was installed for this purpose. Consistent difficulties were encountered in its use, however, (Jovanovich, *this report*) largely because a significant amount of water would condense from the effluent of this port.

First Pass. IOO6 was not considered to be a priority port during first-pass operations, and only field photovac measurements were taken consistently (to provide warnings of high TPH concentrations in the effluent system). We sent smaller number of samples to the laboratory for GC analysis of BTEX compounds (Jovanovich, *this report*). In neither case, were the samples corrected for pressure or the condensed liquid in the sample containers (steel spheres were used). The results of these two analyses are compared to the calculated TPH values obtained previously by using the recovered gasoline from the carbon trailer. With the exception of one errant point at 18 days, the laboratory BTEX measurements of BTEX data track reasonably well the TPH trend measured by Photovac or carbon trailer recovery. On day 18, the large increase in TPH is not reflected in the laboratory BTEX or carbon trailer trends. This point could represent a poorly cleaned sphere. All of the photovac data must be considered to have high average error due to the field measurement. Unfortunately, the laboratory BTEX measurements were not conducted during days 20–33. We made two additional measurements on days 34 and 35.

The difference between the IOO6 measurements and the carbon trailer values may represent the effects of the condenser and demister removing gasoline from the vapor stream. Times at which the IOO6 value for TPH exceeds the carbon trailer value (days 10–14, 24–26 30–31) should correspond to removal of gasoline condensate from the vapor stream, which should show up in the oil water separators (Figure 5 bar data). Only the pulse at days 10–14 unambiguously occurs in the condensate data. Other large excess of gasoline condensate were recovered at day 21 and day 36 (Figure 5) but are not reflected in the photovac data. There is a much better correlation between the photovac excess TPH data shown in Figure 7 and the percent gasoline measured in the condensate recovery tank (Figure 5).

Photovac measurements roughly equate to ppm HC, but laboratory measurements were only made of total BTEX compounds. The first-pass data is subject to a great number of uncertainties, so attempts at calculating a first pass mass balance for Port IOO6 would be speculative at best. Only during days 11–14, when large recovery rates were noted in all streams (this was initial steam breakthrough; Siegel, *this report*) does the data appear to warrant any detailed attention. During this period, the concentration of gasoline at IOO6 was roughly twice that at VESI. On those days, the carbon trailer recovered an average of 44 gallons per day. A total of 115 gallons were recovered from the oil-water separators, or about 29 gallons per day. Given the large errors associated with all the measurements, this value agrees well with the IOO6 measurements. The lack of recovered gasoline during days 23–35 and 30–31 may mean that the IOO6 and percent condensate measurements can not be trusted, or that condensed gasoline was failing to be recovered in the oil-water separators. Again, using the approximate estimate of multiplying the observed carbon trailer recovery rate by the excess in IOO6 values observed, we obtained the following values:

days 25–26, 3×36 gpd (observed average rate) = 98 gal/day;
day 31, 2×46 gpd (rate) = 92 gal/day.

These values would suggest that over three days, 280 gallons of condensate should have been noted: no condensate was observed during days 25–26 and 85 gallons were noted on days 35 and 36.

Another approach would be to directly compare the photovac values obtained at VESI and IOO6 on the same day, using the same instrumentation. Jovanovich (*this report*) presents that comparison, which shows the values track each other closely except as noted:

days 11–13

VESI 3000–2500 ppb

IOO6 1000 ppb higher

day 19

VESI 1500 ppb

IOO6 1700 ppb highe

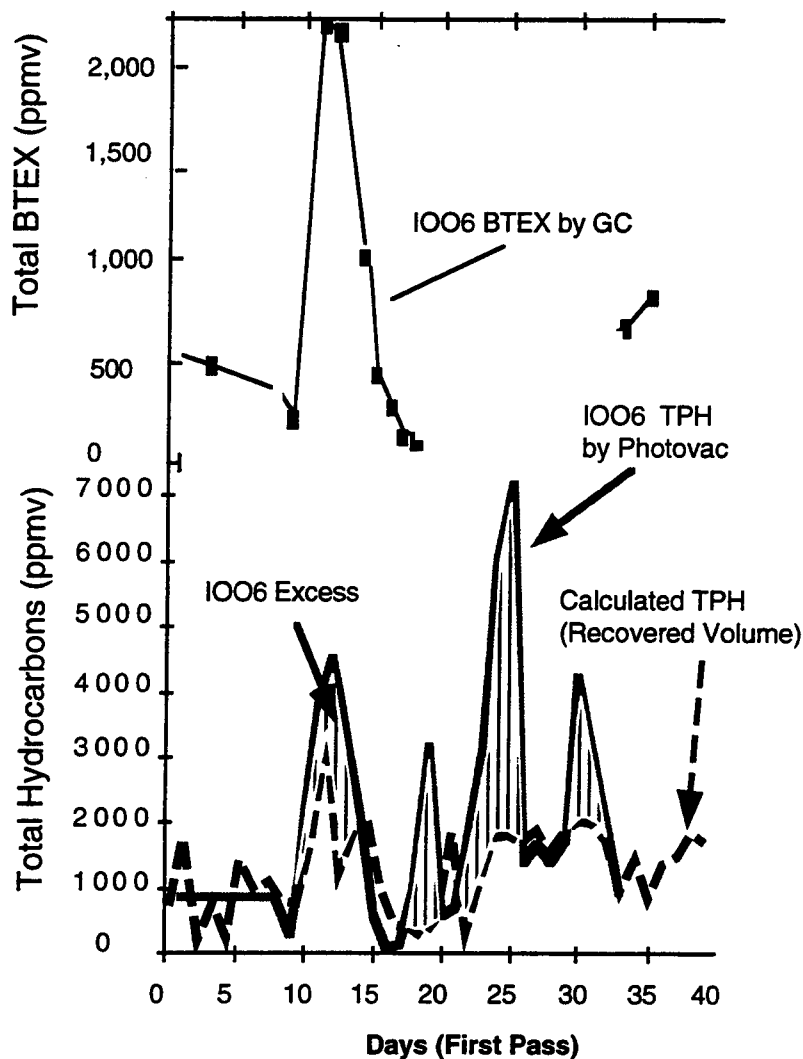


Figure 7. Measurements at Port IOO6 during the first pass (top trace and lower solid trace), compared to the calculated concentration of recovered gasoline from the carbon trailer (lower dashed trace, from Figure 4). BTEX measurements were made by GC in the laboratory (Jovanovich, *this report*). Photovac measurements are a field measurement made by portable GC.

days 23-25

VESI 3000-7000 ppb

IOO6 1500-2000 ppb higher

day 33

VESI 5000 ppb

IOO6 4000 ppb lower.

These values also correspond well in time to the observed peaks in the fraction of gasoline in the condensate (Figure 5), but do not correspond to the recovered gasoline in the oil-water separator.

The calculated HC values for the first-pass vapor are questionable, since there are a number of assumptions inherent in the calculation. Principal among these is the assumption that the carbon trailer was recovering all the gasoline that entered the system. However, the BTEX measurements reported by Jovanovich should be very accurate. As shown in Figure 6, these data require that either the BTEX content of the average vapor for the first pass was very high (57%), or that additional product escaped uncounted. The 56% value is not inconsistent with the initial 60% value noted in the groundwater at UVI, but is much higher than soil or later water chemistry values (see below).

These data do not strongly support the hypothesis that large IOO6 values should be reflected as condensate, but the error in the overall (conceptual) mass balance is only on the order of several hundred gallons. Again, should this amount of gasoline have been passing through the oil-water separator and the UV machine, it should have appeared in an increased UVI value. A mass of 98 gallons per day of gasoline in the average 70,000 gallons per day of water pumped would be slightly more than one part per thousand of gasoline in the water—about twenty times the observed value in the UVI port. Only gasoline present as a separate phase could have been missed at the UVI port. During the first pass, the gasoline at the UVI port should have been saturated with gasoline, since some free product gasoline was always allowed to remain in the oil-water separators. No TPH data were collected during this period, but there were small maxima in the BTEX data (Jovanovich, *this report*). During the first pass, no checks were made for free-product gasoline at this point. In the second pass, we used Sudan IV dye to check for free product in the water recovered at this point (Jovanovich, *this report*), but it was not detected. We cannot at this time resolve these discrepancies in the first-pass data, but the second-pass treatment system modifications appear to have resolved the issue.

Second Pass. Without further concentration data or evidence of the presence of the gasoline at the effluent ports (E006 or CFO), the first-pass mass balance on the vapor stream could not be closed. This led to major revisions in the construction and analysis of the effluent treatment system for the second pass. The condensate stream was completely separated from the aqueous stream [Figure 1(b)]. The aqueous stream was divertable to 500 gallon tanks to check for free product; these two actions may have canceled each other out since no free product from the condensate stream now entered the aqueous stream. Port IOO6 should have continued to provide a check on the total mass of gasoline flowing through the system.

Tables 2 and 3 show the results of two periods of evaluation of the effluent at Port IOO6. Until June 10, we analyzed samples without heating the sphere; after that point we heated the sphere to slightly above the sampling temperature (in the vapor line) before the gas was extracted. Thus, in the unheated samples, the sampled vapor should be in equilibrium with liquid; in the unheated samples, the gas should be equivalent to the full mass of water and gasoline in the vapor stream.

It is immediately apparent that the unheated IOO6 samples very closely mimic the gasoline concentrations observed at the IC engines (ICE IN). Since both samples represent the result of vapor equilibration with liquid (in the case of ICE IN, the liquid is presumed to be in the condenser), the values should be similar. The IOO6 values predict slightly less total gasoline than is observed. As would be expected in this case, the samples do not predict the amount of gasoline that should occur in the condensate; the gas sample only records that it was in contact with free-product gasoline, but not how much. Therefore, these measurements are consistent with IOO6 consistently sampling the vapor stream in a fairly accurate fashion.

Table 2. Comparison of second-pass observed chemical measurements at IOO6 and ICE IN, which are on either side of the vapor-stream condenser [Figure 1(b)], and the observed gasoline recovery rates, from those two points in the system.

		Observed Quantities						
	Date	Days	Pre-condenser IOO6 HC (ppmv)	Post-condenser ICE IN HC (ppmv)	Ratio ICE/IN to IOO6	Gasoline condensate (rate/hr)	ICE rate (gal/hr)	Sum ICE, water, cond. gasoline
Unheated at analysis	5/27/93	4	33,000	31,600	95%	3.41	6.44	9.85
	6/1/93	9	18,000	14,300	79%	1.84	6.51	8.36
	6/3/93	11	13,600	13,000	96%	1.79	5.47	7.26
	6/7/93	15	7,240	6,930	96%	0.17	2.67	2.85
	6/10/93	18	13,600	12,150	89%	0.57	4.34	4.91
Heated at analysis	6/14/93	22	28,509	12,650	44%	0.97	4.34	5.31
	6/17/93	25	42,100	13,800	33%	0.23	4.74	4.97
	6/21/93	29	23,600	5,200	22%	3.52	1.78	5.31
	6/24/93	32	34,000	13,300	39%	0.85	4.41	5.26
	6/28/93	36	20,100	7,970	40%	0.45	2.81	3.27
	7/1/93	39	8,550	4,980	58%	3.06	1.74	4.80
Average (heated samples)						1.51	3.30	4.82

Table 3. Mass balance calculations for port IOO6 during the second pass.

		Derived Quantities				
Date	Steam equal to condensate flow cu ft/min (assumes 170°F steam)	Total gasoline if all condensate was steam (vapor) rate gal/hr	Total gasoline if all condensate was liquid water (no steam/vapor)	Difference in rate: Rate if water condensed divided by observed sum (ICE + condensate)	Predicted condensed gasoline difference, from IOO6-ICEIN difference (gal/hr)	Difference predicted vs observed condensate
5/27/93	58	12.02	6.73	68%	0.29	8%
6/1/93	83	12.32	8.20	98%	1.69	91%
6/3/93	83	8.84	3.73	79%	0.25	14%
6/7/93	186	6.52	1.79	98%	0.12	70%
6/10/93	310	16.87	4.86	99%	0.52	91%
6/14/93	175	23.57	9.79	184%	2.85	295%
6/17/93	94	25.48	14.46	291%	5.88	2587%
6/21/93	468	38.70	8.08	152%	4.15	118%
6/24/93	220	32.02	11.26	214%	3.87	454%
6/28/93	340	26.00	7.08	217%	2.39	527%
7/1/93	450	13.64	2.98	62%	0.45	15%
		26.57	8.94	187%	3.26	216%

Quite different behavior was expected in the second set of samples, which were heated before analysis. First, since the gas injected into the GC was now composed of inert gas (air), water (steam), and gasoline, the total volume that the measured concentration should be applied to is now the volume of the uncondensed gas stream. This is composed of both the inert gas, gasoline, and vaporized water (steam) being extracted and should be commensurately larger than the volume of the vapor stream after the condenser. The average extraction temperature was 170°F, which is 20–30 degrees lower than the boiling point of water at the vacuum pressures used in the second pass. When converted to steam, the amount of water observed in the condensate system would correspond to 94 to 468 scfm of vapor (Table 3, second column). With the observed concentrations of gasoline, these vapor rates predict much larger amounts of total gasoline than observed. (Compare Table 3, third column, to Table 2, last column.) When all the water is instead considered to be condensed (i.e., no steam present in the vapor, only water droplets), the IOO6 values still overpredict the total gasoline recovery by a substantial amount (on average 187% of observed, Table 3 fifth column). Condensate is greatly overpredicted by any model that assumes that there is a large amount of condensable vapor impinging on the heat exchanger [Figure 1(b)]. The volume of gasoline that would be predicted to be condensed and recovered from the oil-water separator is shown along with the ratio to the actual value in the last two columns of Table 3. On average, the second set of samples predicted 216% more gasoline in the condensate than was observed.

The discrepancies in the heated values may arise from the pressure correction applied to the steel spheres (Jovanovich, *this report*). However, this would not be sufficient to explain more than about 30% of the observed deviations. If, however, the gas stream sampled at IOO6 is actually composed mainly of inert gas and water/gasoline droplets, the heating of the sphere during analysis would vaporize those droplets and create a gasoline-rich vapor not representative of the volume in the extraction lines due to the higher vapor pressure of gasoline compared to water. This effect must be studied further before any specific cause can be attributed, but it is clear that the IOO6 values from the second pass do not constrain the overall mass balance of the system.

Perhaps the most interesting result of these analyses is the requirement from all chemical measurements at IOO6 that the steam sampled be composed of inert gas and condensed liquids. This is consistent with the temperatures observed (Siegel, *this report*). Although the liquid water was routinely at the predicted boiling temperature for liquid water under the applied pressure, the temperature of the vapor stream was always below that point. This may be explained by cooling and equilibration with ground-water temperature in the extraction well (Figure 8). The air pumped down to the air-lift pumps traveled in an uninsulated steel pipe; over a distance of 100 ft, it could transfer most of the heat difference between it and the upward-moving extracted vapor (a better counter-current exchanger probably could not have been constructed). In addition to this, some cooler air may have been entering the top of the screened zones particularly in GSW 16, which was screened as shallow as 40 ft. Balancing these cooling effects was the flow of hot water up the extraction pipe. The extracted water temperature could not exceed the boiling point at the applied vacuum in the well, and because of its greater mass, the temperature of the extracted water does not change significantly during transport up the well bore. Figures 9(a), (b) and (c) show the temperature of the pumped water and extracted vapor in the three phases, compared to the calculated boiling point of water at the observed vacuum.

In Figure 9(a) the first-pass temperature of the extracted fluids is rigorously limited to the boiling point at the applied pressure [Figure 9(b)] the temperature of extracted vapor and water does not quite reach the boiling point. In the second pass, the applied vacuum on the wells was much lower than in the first pass, and total volume flow rates about 1/3 of the first-pass rates. These lower values may have permitted non-equilibrium pressures to occur in the system, as condensation occurred in the well bore or in the condenser. In the ARV phase [Figure 9(c)], the clearest indication of the heat exchange mechanisms downwell is seen. The vapor temperature rigorously follows the extracted water temperature even though both are far below the boiling point. At the end of the ARV, the water pumps were shut off, and the vapor temperature instantly jumps 30°C. This apparently is the actual vapor temperature in the formation. Temperatures for well GEW 808 are used in this comparison; vapor from this well was consistently hotter than from the other wells.

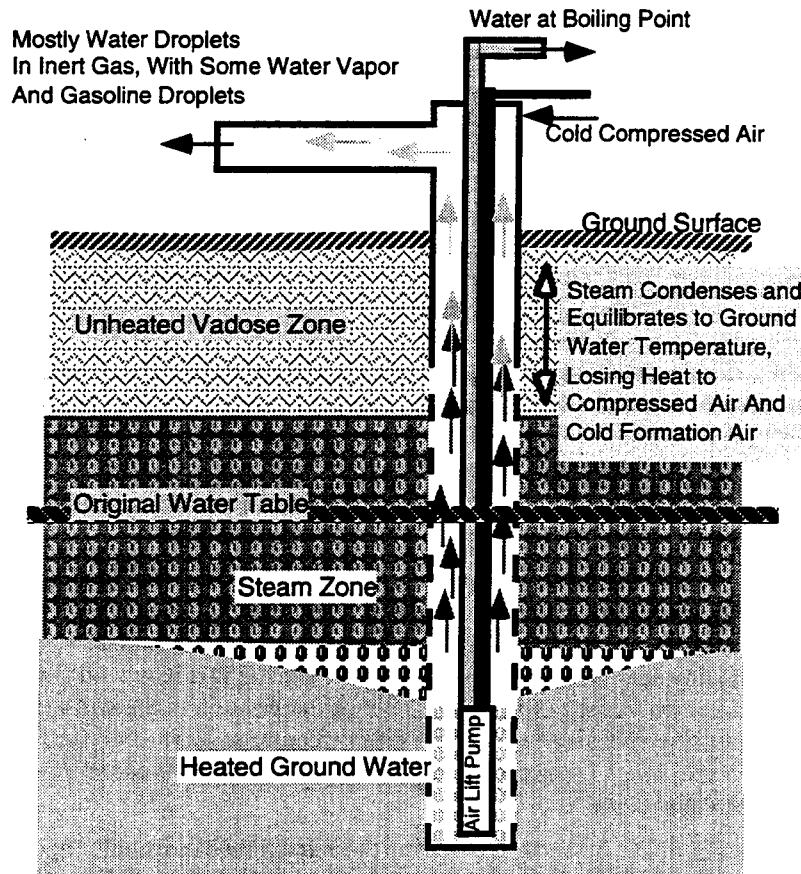


Figure 8. Schematic view of the heat-exchange mechanisms occurring in the extraction well.

The volume of extracted condensate goes up dramatically in the first two passes when the temperature of the vapor reaches the temperature of the pumped groundwater, even if the boiling point is not reached in uphole temperature measurements. One example of this is seen in the initial first-pass breakthrough at day 12. This phenomenon may be also caused by steam entering the well, along with slightly cooler water. Again, as the steam condenses it forms droplets that are carried in the air flow to the surface facility but at the temperature of the non-boiling groundwater.

The result of the down-hole heat exchange mechanism appears to be that most, if not all, of the extracted steam was condensed before it reached the surface. This is very important for future treatment systems in that it would suggest that the large surface cooling capacity present at the gas pad is not needed to condense steam. This is probably only applicable to deep sites, however.

Temperature and Extraction Rates - First Pass

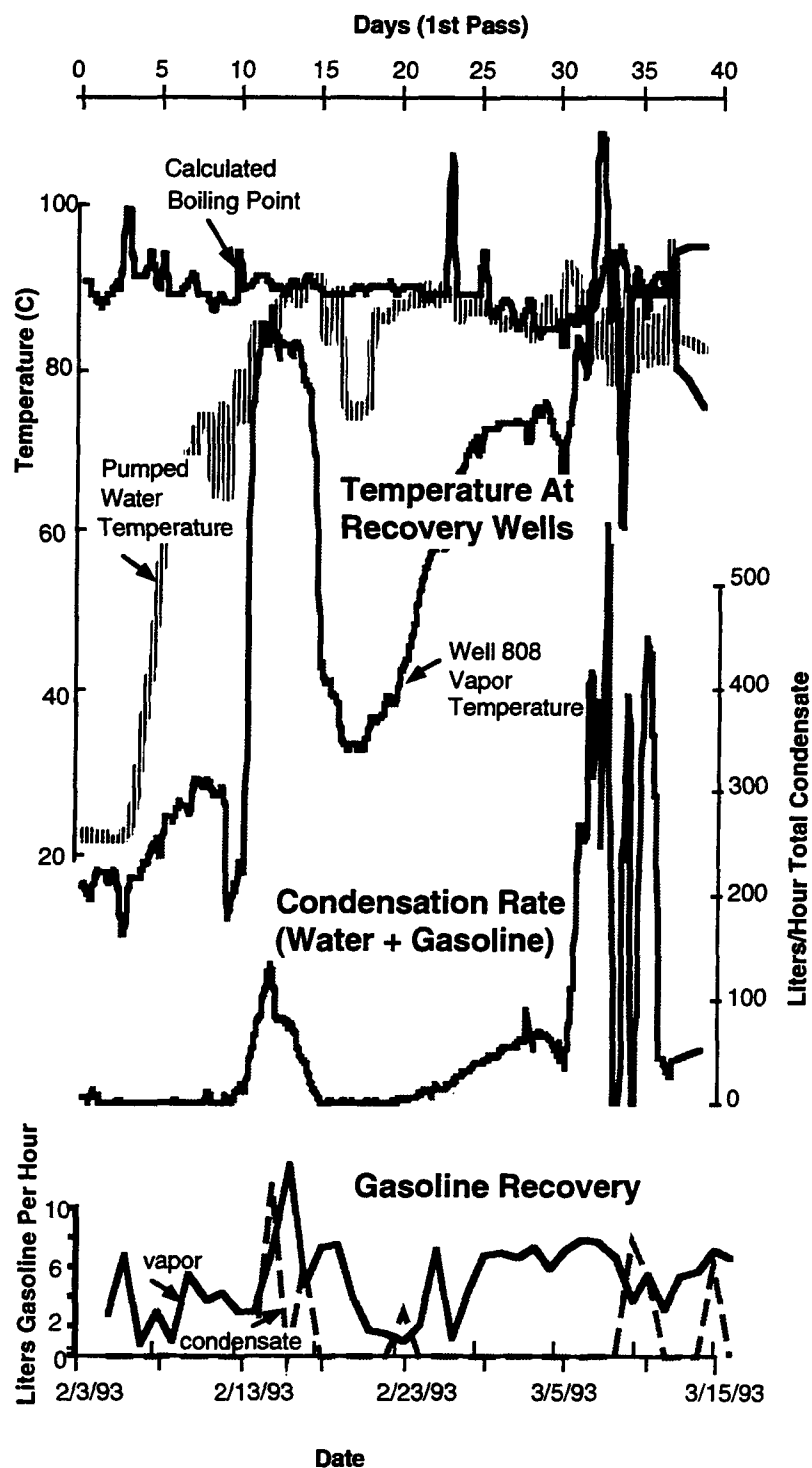


Figure 9(a). First-pass extraction temperatures, rates of accumulation of total condensate, and gasoline recovery rates from the vapor and condensate streams. Calculated boiling points from the steam tables, in *Handbook of Chemistry and Physics*, CRS Press (1974). Two occasions where the calculated boiling points are seen to rise above 100°C are due to pressurization of the extraction system when the carbon trailer system pump failed. The wells were quenched with cold water at that point (the vapor system was not designed to be under pressure, just vacuum).

Temperature and Extraction Rate Summary - Second Pass

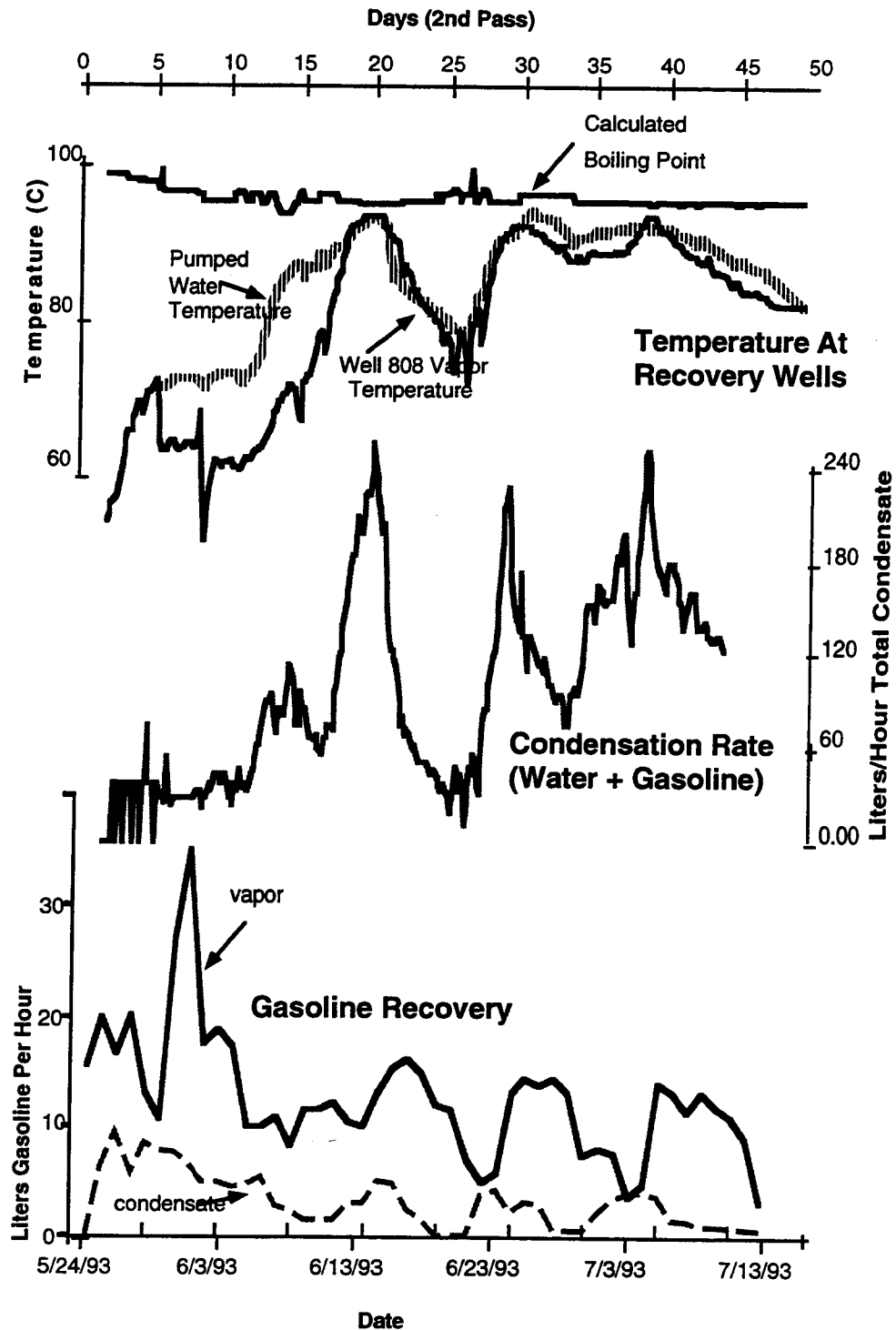


Figure 9(b). Second-pass extraction temperatures, rates of accumulation of total condensate, and gasoline recovery rates from the vapor and condensate streams. Scaled to approximately the same time and extraction rate/temperature scales as in Figure 9(a), although absolute values differ. Groundwater pumping began on day 5 of the second pass.

Temperature and Extraction Rate Summary - ARV Phase

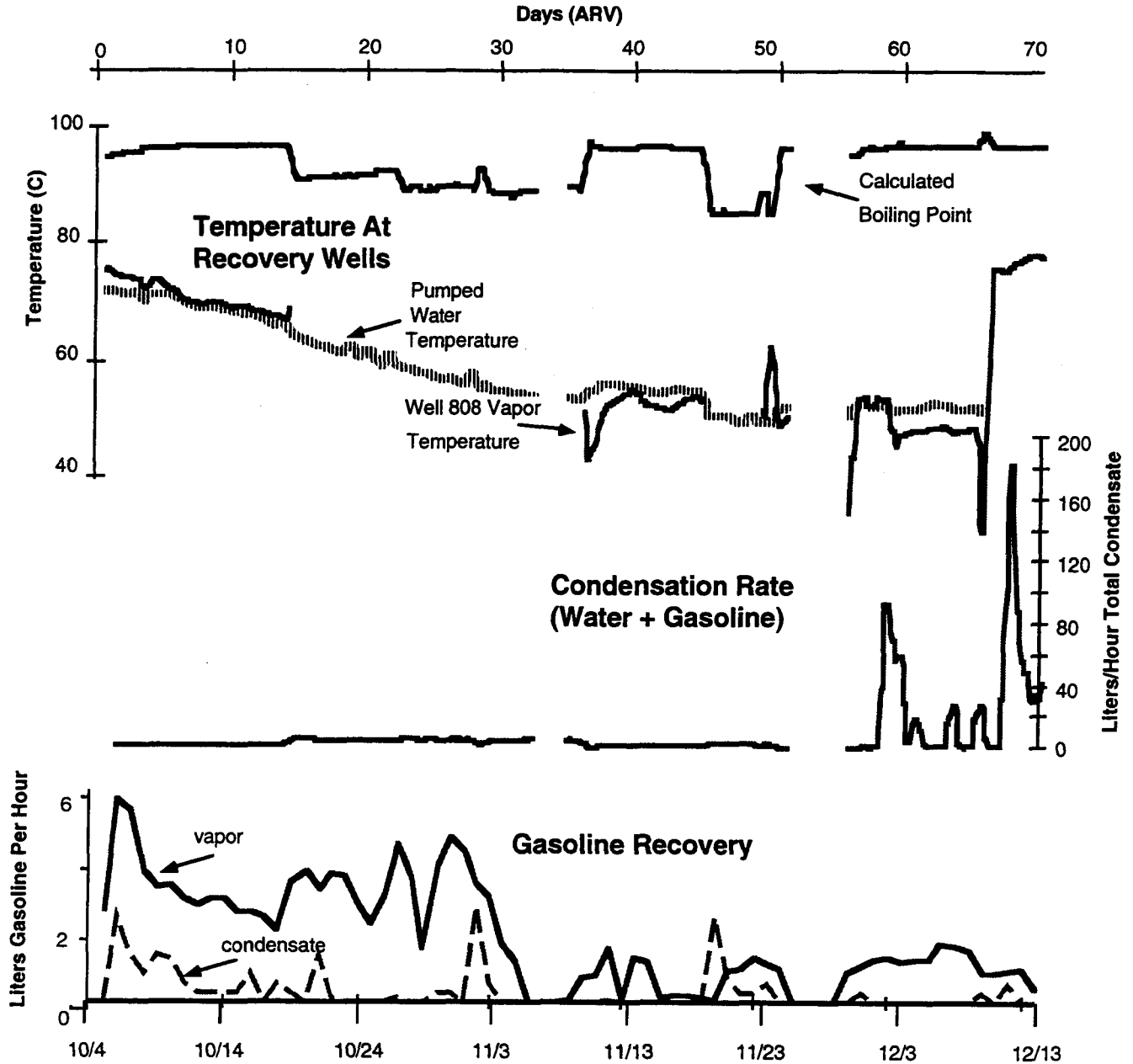


Figure 9(c). ARV extraction temperatures, rates of accumulation of total condensate, and gasoline recovery rates from the vapor and condensate streams. (Sweeney et al., *this report*). Scaled to approximately the same time and extraction rate/temperature scales as in Figure 9(a), although absolute values differ. Vapor data are only shown when well 808 was turned on. Calculated boiling point changes significantly as different wells, with different flow rates, were used in this phase. Condensate recovery jumped at the end of ARV due to electrical heating (Sweeney et al., *this report*)

Groundwater

The total amount of gasoline in the pumped groundwater was a very small (about 30 gallons per million gallons of pumped water). We calculated this amount from the SEPI concentration data and the water pumped water volume for each day. The calculation method was the same for all three passes. We have assumed previously that the liquid gasoline recovered from the oil-water separators in the first pass actually came from the condensed vapor stream, since no gasoline was recovered there during the second pass.

Original predictions of the Dynamic Underground Stripping process indicated that significant amounts of gasoline would be recovered in the liquid stream, carried in front of the steam zone as a "condensate front" (Udell, *this report*). The chemistry data presented here, however, show no evidence that liquid gasoline was recovered along with the pumped groundwater. This may be due to the differing times of steam breakthrough to the extraction wells from each injector, and the presence of multiple recovery wells. Any large amounts of liquid gasoline near the extraction wells would have been readily vaporized and removed in the vapor stream. The boiling of water in the well-bore would also enhance the transfer of liquid gasoline into the vapor phase. The total gasoline recovered in groundwater is calculated as follows:

$$\text{Gallons gasoline/day} = \text{SEPI concentration (mg/L)} / 1000 \text{ mg/g} \times \text{water pumped (gal)} / (0.2426 \text{ gal/L}) / 737 \text{ g gasoline/L} \times 0.2426 \text{ gal/L}.$$

Errors in this calculation are associated with the volume of water pumped (measured by a standard water meter and assumed to be precise to the volume reported, but not independently checked) and the analytical error. Figure 10 shows the results of aqueous chemistry measured during the later part of the second pass, when the chemistry was not changing rapidly (Jovanovich, *this report*). There is an offset between SEPI and UVI in both categories, possibly due to air stripping in the oil-water separators. There is also the possibility that some active biological degradation occurs in the piping and oil-water separators. The variability in this offset should be a good indicator of the overall analytical error of this method; it appears to be no greater than 10%. Since this is a measurement of the mass of gasoline, there is some error associated with the conversion to volume of liquid. A reference mass/volume of 737 g/L was used, (Lyman et al., 1991) but this may vary by 5% based on the weathering and initial composition of the gasoline.

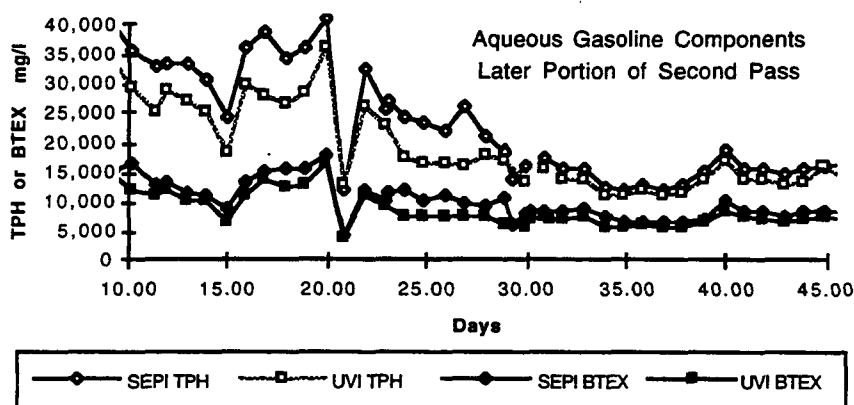


Figure 10. Aqueous stream gasoline composition measured at two consecutive points, from spreadsheet Dynamic Underground Stripping 2nd Pass AQ (M. Jovanovich).

The estimated total error in this measurement is then 10% + 5% (independent errors) and the total gasoline extracted in the aqueous phase during the second pass is approximately equal to 106 gallons \pm 15 gallons.

First pass: 159 \pm 20 gallons

Second pass: 106 \pm 15 gallons

ARV: 59 \pm 7 gallons

Gasoline Chemistry

The mass balance calculations used in a number of gasoline extraction reports are dependent on the chemical makeup of the contaminant (Lyman et al., 1991; Devaney et al., *this report*). Often benzene or BTEX values are used because they are more readily measured and because the BTEX compounds are the regulated species. Jovanovich (*this report*) extensively discusses the variation in chemistry of the extracted fluids, and Devaney (*this report*) discusses the related inhomogeneity in the gasoline compositions analyzed during the characterization phase. In this section, we discuss the changes in overall chemistry of the gasoline extracted during Dynamic Underground Stripping, and its implications for the different removal mechanisms that can occur as part of the process.

Our goal of this analysis was to understand some of the changes in chemistry of extracted gasoline by using the ratio of benzene to TPH (total petroleum hydrocarbons). Benzene is one of the more volatile components of gasoline, particularly gasoline that has been in the ground for several years and has lost the extremely volatile C4 and C5 hydrocarbons. (Lyman et al., 1991) It is also one of the most soluble and least sorbed components. Thus the ratio of benzene to TPH can be expected to reflect processes involving volatilization, solution, or sorption.

Cook et al. (1991) made the assumption in their analysis of the vacuum extraction tests conducted prior to Dynamic Underground Stripping that the overall BTEX content of the gasoline present at the site was 27.5%. While this value is fairly high, it is within the range of common gasoline chemistries (Lyman et al., 1991). This value is critical to evaluating the vacuum venting results, which were only obtained in terms of BTEX compounds.

Cook et al. noted that post-vacuum-venting soil cores indicated that BTEX compounds were preferentially removed from the soil around the vent. If this type of fractionation occurs during any extraction method, it will significantly affect the apparent extraction efficiency.

A common question is the relative "solubility" of gasoline in water. Gasoline is a multicomponent fluid whose solubility is in fact a complex partition function between water and the gasoline constituents. As such, a large variability may be expected; Lyman et al. (1991) report values from 30,000 to 120,000 ppb ranging from highly weathered to fresh gasoline. During the second pass, the "solubility" of the condensed gasoline in water was accurately measured by the MEGA AQ sample port. The water in this oil-water separator unit was always in intimate contact with free product, but the chemistry of that free product changed over time. Jovanovich (*this report*) shows that the average value for TPH in this water is about 85,000 ppb and for BTEX 35,000 ppb. However, early in the second pass, the TPH value was as high as 150,000 ppb and the BTEX value 45,000 ppb.

Soil Chemistry. Very few measurements of total petroleum hydrocarbons have been made at the gasoline spill site. BTEX measurements (coupled with 1,2 DCA and EDB) have been widely used to pinpoint contaminated areas, since they are the only regulated compounds (Dresen et al., 1986). Although Cook et al. refer to TPH measurements after vacuum venting, the only TPH measurements in the LLNL database before vacuum venting and Dynamic Underground Stripping are for wells GSW 445, GSW 006, and GSW 015 (Dresen et al. cite two data points for GSW 443 as well). GSW-015 was extensively characterized, including many TPH measurements (Figure 1). It lies in the center of the spill area. Nichols et al. concluded that approximately 16% of the soil gasoline was BTEX., and Devaney (*this report*) used an average value of 8% xylene in TPH for soils. Table 4 shows the analyses of TPH and benzene for wells GSB 015 and GSB 445. Notably, above 50 ft in GSB 015, there is a dramatic decrease in benzene content; this is presumably due to both loss to the atmosphere and biologic activity.

Table 4. Pre-treatment soil analyses of TPH and benzene.

Well depth (ft)	GSB-015 soil		Ratio
	TPH (ppm)	Benzene (ppm)	
22.2	4800		
24.8	7500	8.4	893
27.8	3700	7.8	474
36.7	700	1.6	438
39.4	2900	13	223
42.7	8100	8.5	953
45	600	1.2	500
48.7	290	1.3	223
51.8	6600	130	51
54.2	3800	55	69
57.1	140	1.2	117
59.4	3100	37	84
62.4	11000	130	85
66.1	5200	110	47
69.3	3700	46	80
74.3	1400	5.7	246
77.5	2900	60	48
80.5	6900	140	49
83.5	900	9.3	97
86.5	370	0.8	463
92.8	1700	34	50
93	1100	9.3	118
101.3	1800	25	72
103	1200	16	75
106.3	2400	18	133
109.3	710	9.1	78
110.5	1200	14	86
113.8	89	0.3	297
115.2	470	7.3	64
120.3	5100	64	80
121.5	400	6.2	65
Weighted average of ratios below 50 ft.			81
GSB-015 water			
9-Mar-88	11000	2200	5
8-Jun-88	39000	9500	4
8-Jun-88	33000	5800	6
9-Sep-88	9000	2100	4
8-Sep-88	13000	3400	4
GSB-445 soil			
30-Nov-87			
90.5	210	2.3	91
119.8	1600	17	94
Weighted average of ratios below 50 ft.			93

One of the Dynamic Underground Stripping characterization wells was analyzed for TPH; TEP 10 is near the vacuum extraction experiment area, and also shows a very high TPH/benzene ratio in the vadose zone affected by the venting (Table 5). Cook et al. note that the venting was apparently not effective below depths of about 90 ft, apparently due to clogged well screens or the presence of free product.

Table 5. Dynamic Underground Stripping characterization soil analysis of TPH and benzene.

TEP 010 soil		17-Mar-17	
55.8	1800		
77.3	500		
94	3700	3.6	1028
103.5	700	59	12
107.8	500	9	56
110.3	8000	87	92
Weighted average of ratios below 100 ft			84

Table 4 also shows the corresponding TPH/benzene ratios for water collected from GSW-015 soon after drilling; benzene is preferentially partitioned into the aqueous phase. The average soil values are obtained by weighting the observed ratio in each sample by the amount of TPH. These weighted averages yield a value of approximately 1 to 1.2% benzene in the gasoline contaminant.

This discussion uses the benzene-to-TPH ratio because it is sensitive to physical processes that occur during Dynamic Underground Stripping. However, the uncertainty in the overall mass balance at the site is reflected by the scatter in Figures 11 and 12; because of the extreme paucity of historical TPH data, the uncertainty in the original inventory is very large. Based on the scatter in the xylene data, it is reasonable to assign an uncertainty of at least $\pm 50\%$ of the total gasoline present (Devaney, *this report*). At a future time it may be possible to use the existing benzene and xylene data independently to obtain a mass balance on just those components; this may be a more accurate assessment of the total removal of contaminant than the total gasoline values we have used.

Extracted Vapor Chemistry. Vapor extracted from soil undergoes fractionation (the more volatile components are removed first), whether the gasoline contaminant is present as free product or dissolved in water (Lyman et al. 1991). Significant fractionation was observed by Cook et al. in their venting experiments at the gasoline spill site. The effective difference in vapor partial pressures among the gasoline components is maintained as temperature increases (Udell, *this report*, Figure 4). This would indicate that if gas is removed by the same type of fractional distillation mechanism, benzene should again partition into the vapor phase. However, if instead a mass-removal mechanism is operating (Udell, *this report*), such as the conversion of an entire volume of fluid into vapor, the ratio of benzene to TPH in the extracted vapor will reflect the original contaminant.

The observed and calculated vapor compositions from the first pass were given in Table 1, and benzene/TPH ratios are plotted in Figure 13. This figure shows that during the first pass, there seems to have been some fractionation in the vapor phase toward volatile (benzene)-rich compositions. Although the total petroleum hydrocarbon content of the first-pass vapor is subject to considerable error, the benzene concentration is significantly higher than the observed soil contaminant composition of 1-2% benzene. The highest concentrations occurred at the point of initial steam breakthrough to the extraction wells. Data for benzene concentration are not available for most of the latter half of the second pass (only day 35).

During the second pass, the TPH content of the vapor was accurately determined (Jovanovich, *this report*). Figure 14 shows two types of behavior in the second-pass vapor measured after the condensing system [at ICE-IN, Figure 1(b)].

The composition of the majority of the gasoline recovered in the vapor phase falls directly onto the original soil chemistry (Figure 11). During this phase, the system was optimized for removal (Udell, *this report*, Siegel, *this report*). Most of the target volume was at or near steam temperature, and significant boiling of the formation was occurring. Removal seems to have occurred with very little fractionation during this period.

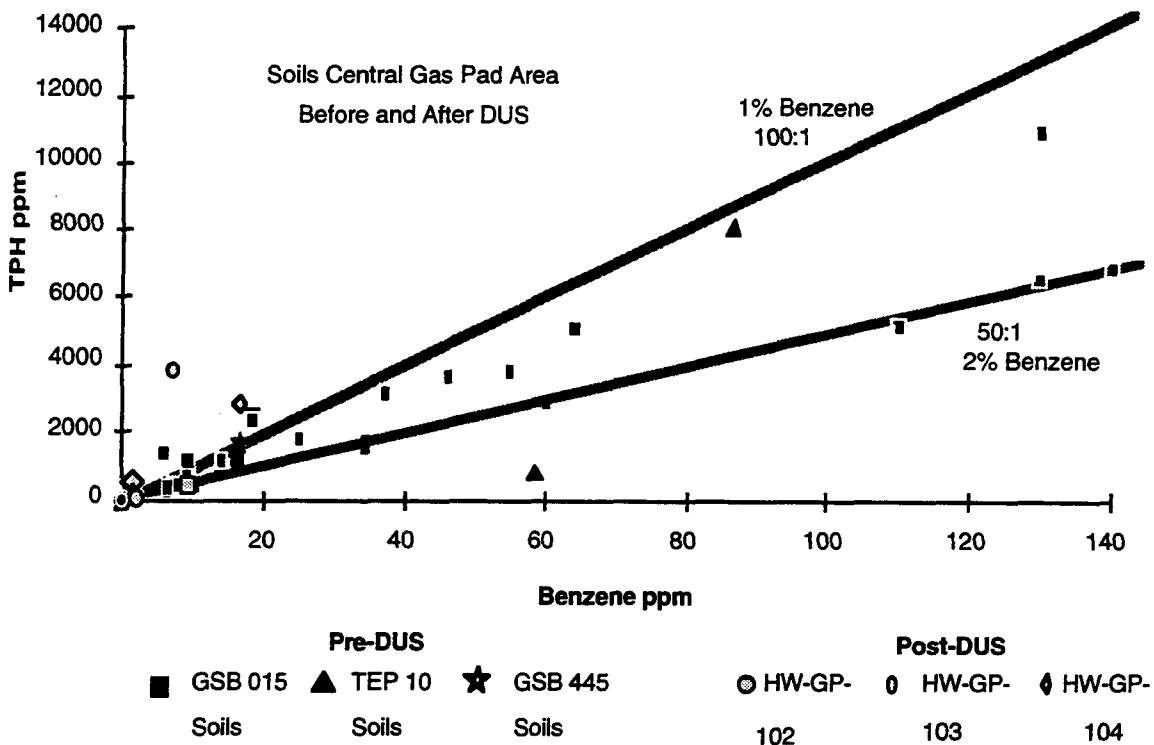


Figure 11. Ratio of total petroleum hydrocarbons to benzene observed in soils at the gasoline spill site before vacuum or Dynamic Underground Stripping treatment (filled symbols) and after Dynamic Underground Stripping treatment (open symbols). TEP 10 was sampled between the vacuum venting and Dynamic Underground Stripping phases. A consistent trend of around 1% benzene is maintained for all but HW GP 103, which was located in the free-product pool around the central extraction wells after the second pass.

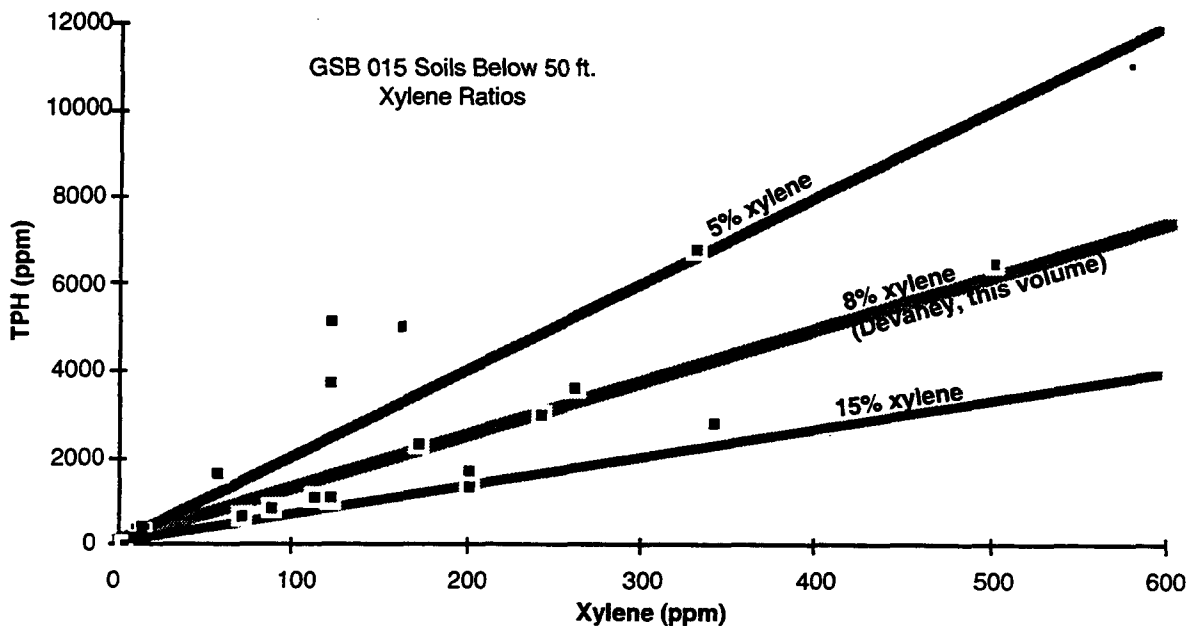


Figure 12. Ratio of xylene to TPH below 50 ft in original boring of GSB 015 (same data-set as the GSB 015 data in Figure 11). The value of 8% was used by Devaney (*this report*) to estimate the total gasoline contained in the treatment area.

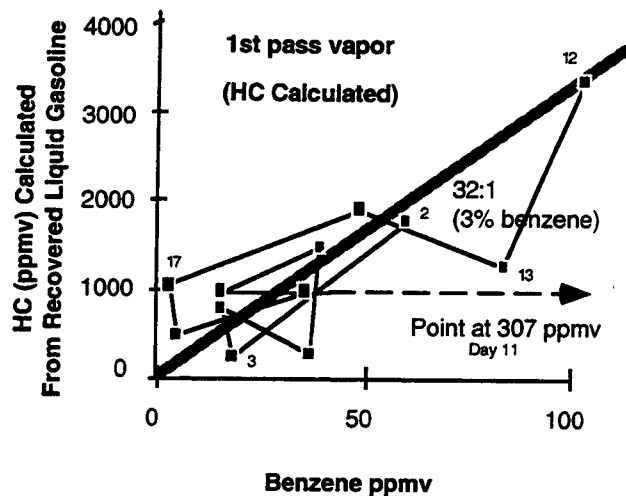


Figure 13. TPH-to-benzene ratio of extracted vapor during the first pass. TPH (HC) value calculated from recovered gasoline amount (Figure 4). One additional point lies at highly enriched benzene values (310 ppm benzene). Sequential data points are connected by connecting lines, day numbers for the first pass are noted. Breakthrough occurred on days 11 and 12.

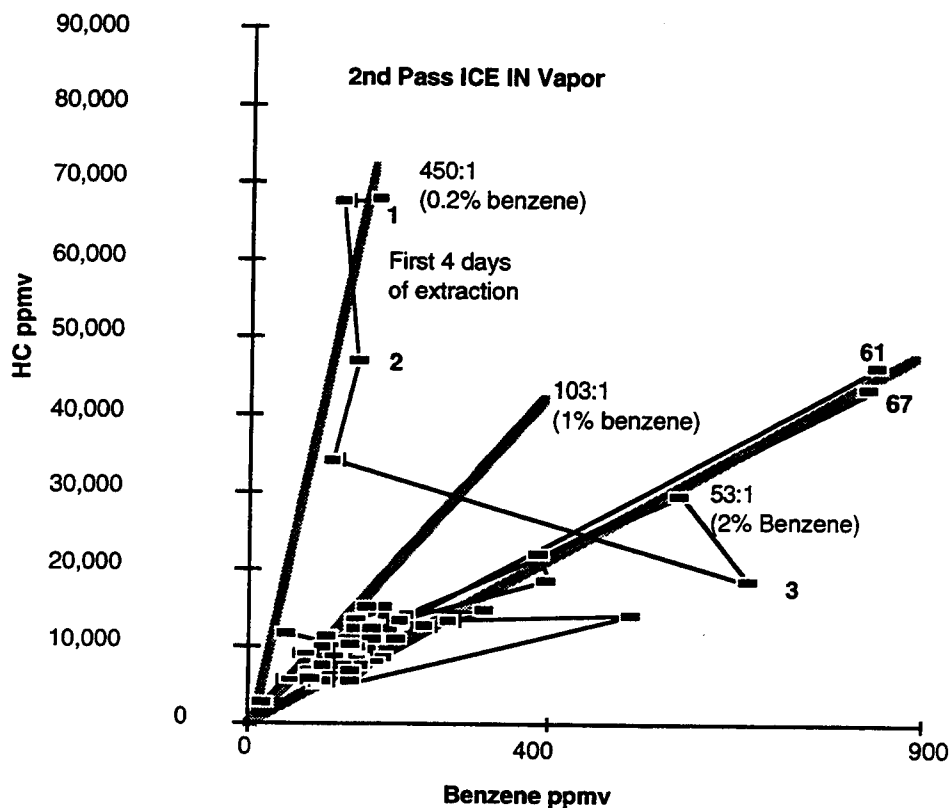


Figure 14. Composition of extracted vapor during the second pass and occasional vapor extraction between the second pass and ARV phase. Sequential data points are connected; first three days are numbered. Extraction on days 61 and 67 occurred after groundwater pumps had been shut down for several weeks at the end of the second pass.

The first four days of the second pass resulted in unusual chemistry, however, in both the vapor and aqueous phases (see below). The benzene content of this vapor was extremely low (0.2%), and it contained an anomalous amount of very light hydrocarbons (Jovanovich, *this report*) requiring the hydrocarbon analysis range to be extended down to C3 from the usual C6-C12 range. Although vapor analyses were not available during the end of the first pass, water analyses (below) indicated that unusual gasoline chemistry was being recovered after the end of steaming. This phenomenon is discussed further at the end of this section (vapor generated during heat soak period). After the end of the second pass (days 61 and 67 of the second pass, if same counting system is maintained), the vacuum extraction system was turned on for testing and control of vapor migration. The vapor recovered on those days is concentrated, but the benzene/TPH ratio is identical to the second-pass values and soil values.

During the final ARV phase, this trend continued. The extracted vapor chemistry changed little from the second pass (Figure 15). The vapor composition trended toward less benzene-rich compositions; at this point, almost 85% of the total gasoline had been removed. This indicates that although some fractional distillation was occurring at this time, it was a minor component of the overall mass removal.

Extracted Water and Condensate Chemistry. The extraordinary range of chemical compositions reported by Jovanovich was not anticipated in planning the chemical sampling for Dynamic Underground Stripping. The first observations of effluent water chemistry (Figure 16) displayed a wide variation. This variation did not seem to be simply a distillation effect, although the fraction of BTEX in total gasoline declined from about 62% to 25% during the first pass (Jovanovich, *this report*).

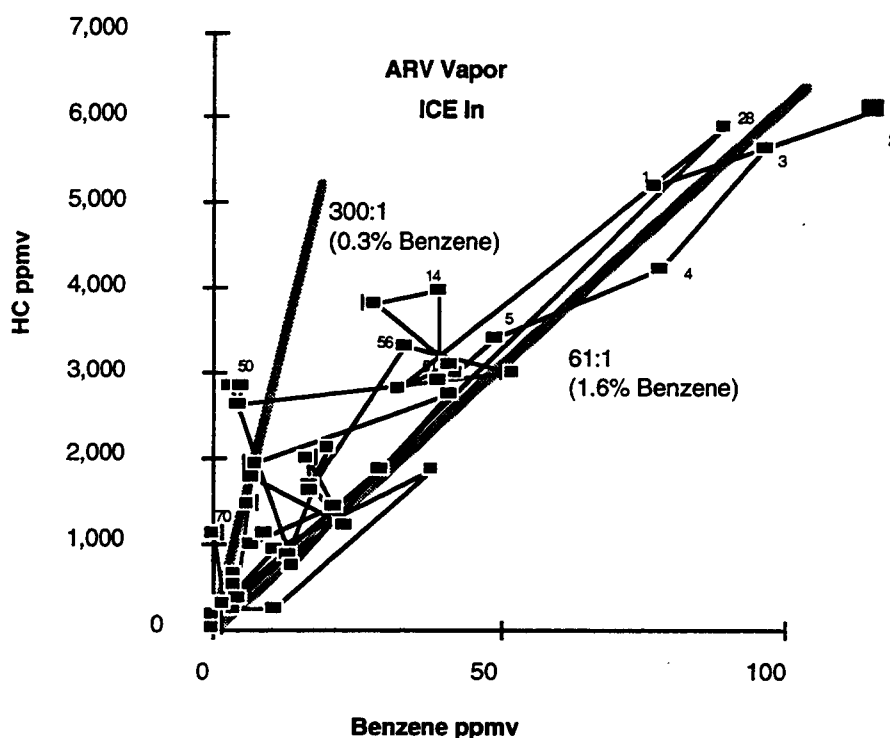


Figure 15. ARV phase vapor chemistry. All days are included without respect for which well was used for extraction (tests were run from the steam injection wells; Sweeney et al. *this report*). Sequential points are linked, days of sample collection are noted for several samples.

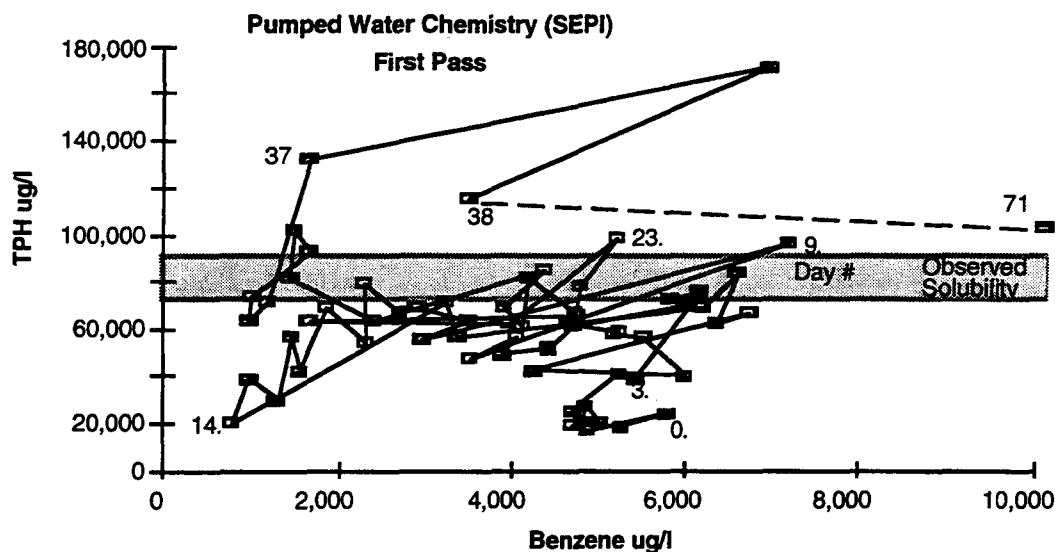


Figure 16. Observed variation in TPH/benzene ratio in extracted water during the first pass. Day numbers in the first pass (Jovanovich, *this report*) are indicated for selected points. The water was sampled more than once on most days. Steam injection ceased at the end of day 36. Operations were discontinued from day 38 to day 71 (the UV system was tested on day 71 in preparation for the second pass). Observed solubility from Jovanovich, (*this report*); this was determined by adding free-product gasoline recovered from the oil-water separators during mid-first-pass to site groundwater.

Much of the water chemistry is delimited by the “solubility” measured by Jovanovich (*this report*) who added 2 mL of gasoline recovered from the oil-water separator to a standard VOA container filled with site groundwater. Seven measurements ranging up to 137 hr were taken and fell in the range of 75,000 to 92,000 $\mu\text{g/L}$ TPH and 2,200 to 2,800 $\mu\text{g/L}$ benzene. The recovered groundwater had much greater benzene concentrations; it is likely that the gasoline recovered from the oil-water separator had already equilibrated with water, and was low in benzene content.

After steam injection and vapor recovery were stopped on day 37, the water chemistry behavior was quite remarkable. Concentrations jumped to above 100,000- $\mu\text{g/L}$ TPH. When the UV/H₂O₂ machine was opened for cleaning after the second pass, it contained several liters of free-product gasoline. Water recovered along with that gasoline from the interior of the UV treatment tubes contained over 200,000- $\mu\text{g/L}$ TPH (but less than 100- $\mu\text{g/L}$ benzene) (Jovanovich, *this report*).

The large chemical variations observed might be due to the physical processes of Dynamic Underground Stripping, or to some effect of sampling different gasoline reservoirs. For instance, the benzene-depleted fuel near the vacuum extraction experimental area could have been recovered first. Figures 17 and 18 show the ranges of chemistry observed in groundwaters in the gas pad area historically (pre-1990) and just before Dynamic Underground Stripping (1990–1992). The historical data include wells sampled within a decade of the presumed spill date. Over time, all sampled wells show a strong trend toward reduced TPH and reduced benzene concentrations that closely follow the modern groundwater trend of approximately 5:1 TPH to benzene.

During the second pass, the liquid stream was fully characterized (Jovanovich, *this report*). The pumped groundwater was isolated from condensate, and all liquid streams were carefully measured. The condensate was separated into two analytical units; water (MEGA AQ) and gasoline (MEGA HC). No free product was recovered from the pumped water. During the second pass and the ARV phase (the treatment system was unchanged between these phases), the condensate system continuously received gasoline, although at a decreasing rate. Therefore the water in the separator (MEGA AQ) was in continuous contact with gasoline and should reflect solubility limits at ambient conditions (roughly 20°C).

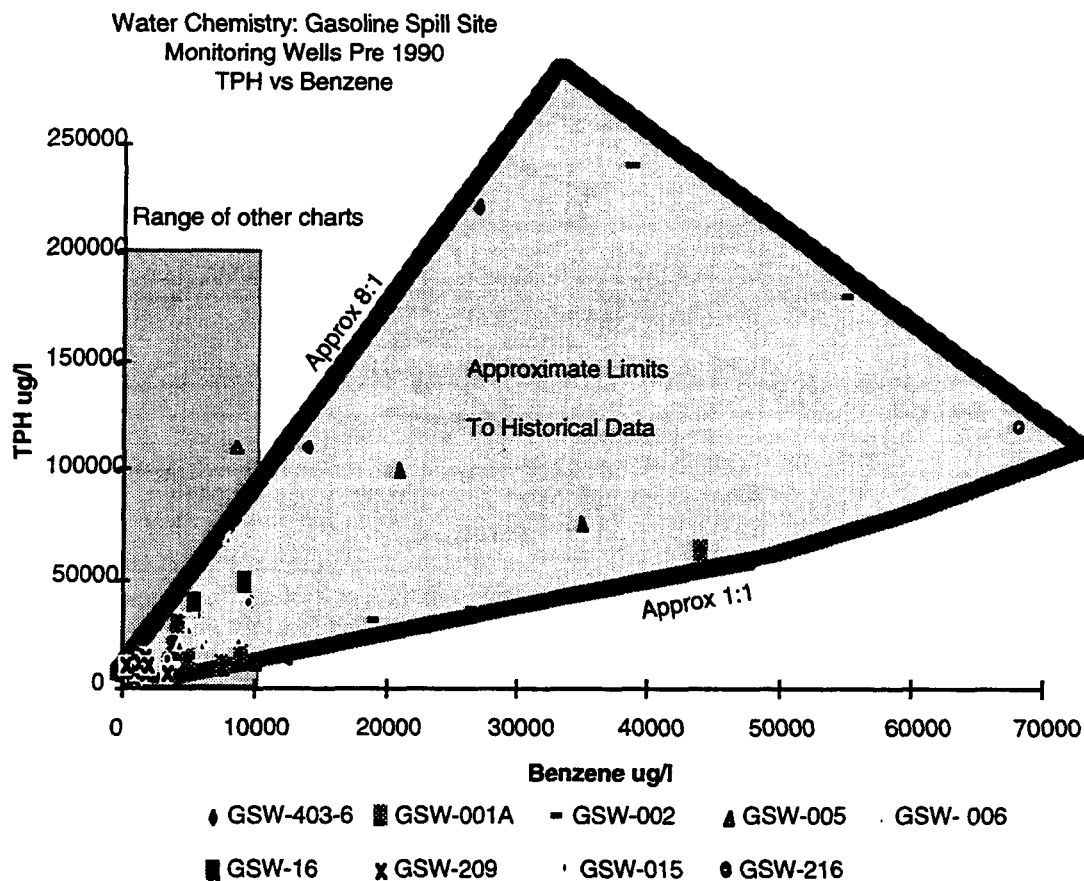


Figure 17. Range of water chemistries observed historically at the gasoline spill site (before 1990). As for soil, the groundwater data are limited by the number of TPH or gasoline fingerprint analyses collected.

The combined analyses for aqueous samples during the second pass and ARV phase (Sweeney et al., *this report*) are shown in Figure 19. Gasoline in groundwater pumped during the second pass (SEPI) falls along a well-defined trend with a slope of about 12:1 (8% benzene), which continues smoothly in the ARV phase. This trend is enriched in TPH relative to the modern groundwater analyses, presumably a function of reduced sorption of the gasoline components and, therefore, increased availability for dissolution. Benzene concentrations are very similar to the range observed before Dynamic Underground Stripping (Figure 18). Sequentially collected points are connected by lines for the second-pass data, and although there is an overall trend toward reduced TPH and benzene, the trend reverses numerous times during the second pass. This has not yet been correlated with physical phenomena observed during steam injection or extraction, but may be related to the “huff and puff” cyclic operation (Udell, *this report*).

Condensed water falls into two distinct fields during the second pass, with a third field defining the ARV condensate. The initial condensate is very high in TPH and one value (day 9) is very high in benzene (7%). After day 15, the condensate has a much smaller TPH content, with similar benzene content to the pumped water (SEPI) at that time. This water falls into the range previously identified as roughly the solubility limit for an average gasoline (around 80,000 ppb) (Figure 16). The initially high concentrations in the condensate roughly correlate with the initially TPH-rich vapor recovered in the second pass (Figure 14), which also had anomalously high concentrations of light hydrocarbons. The first day of condensate from the ARV phase also had a relatively higher TPH content, although the overall concentrations are reduced.

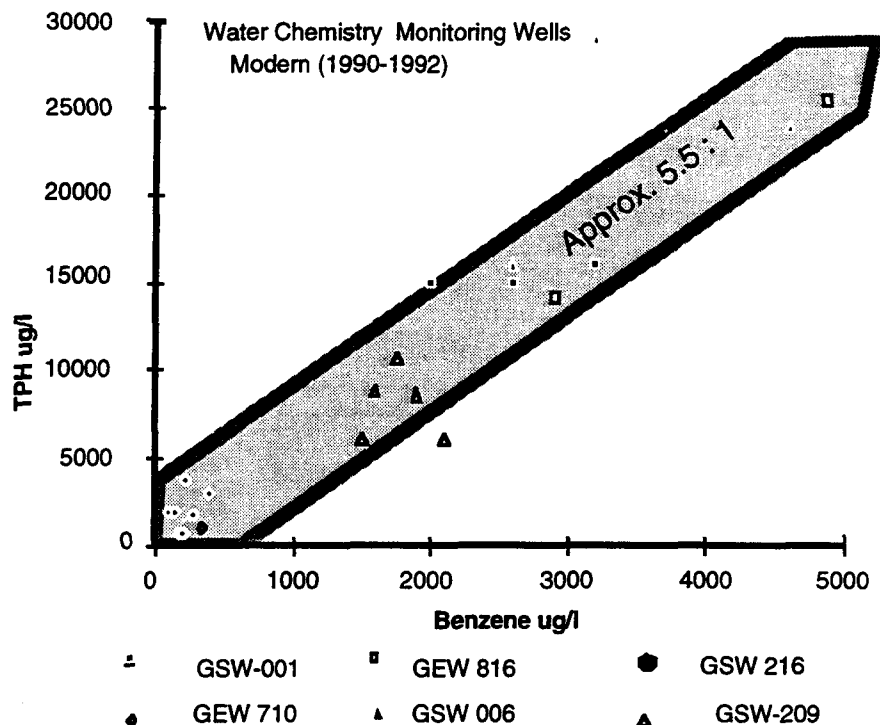


Figure 18. Modern range of TPH to benzene chemistries observed in groundwater at the gasoline spill site (1990-1992) before Dynamic Underground Stripping.

The time sequencing of the SEPI and MEGA AQ data are not exact, since the throughput of water past the MEGA AQ port is on the order of 1/100 that at SEPI. The condensate values from MEGA AQ will retain chemical signature longer than the groundwater values as the water sits in the oil-water separator. However, it is apparent that on a gross scale the condensate has a much higher TPH content but a very similar benzene content to the pumped groundwater at all times. As the overall source of gasoline contacting the water is depleted in benzene (it is being removed at about 10 times the soil TPH/benzene ratio) the groundwater gradually evolves to a higher TPH/benzene ratio. This behavior reflects the very high solubility of benzene in water; it will preferentially enter the aqueous phase compared to other hydrocarbons in gasoline.

The results from the second pass and ARV allow us to revisit the first pass results. Figure 20 shows the first pass results with the fields defined in Figures 18 and 19 superimposed. The effects of the addition of condensate to the pumped water are apparent; the composition of the sampled water begins in the modern, untreated groundwater field and moves to the second-pass trend during heating. It then moves to the solubility limit and fluctuates in between those two trends during the remainder of steam injection. This is most simply interpreted as representing the same trend of pumped water as seen in the second pass, with condensate added in varying amounts. After steam is shut off on day 37, the recovery rates for condensate presumably increased (as was seen in second-pass huff-and-puff operations, Siegel, *this report*, Udell, *this report*). This gasoline-rich condensate was injected into the water treatment system, resulting in very high values at SEPI. The TPH/benzene ratios reflect the unusually TPH-rich vapor that was accumulated at the start of the second pass.

Electrical Heating Effects. A number of groundwater monitoring wells were sampled before Dynamic Underground Stripping, and then after the electric heating phase. They showed chemical compositions very similar to those seen in the second-pass condensate and the later first-pass chemistry

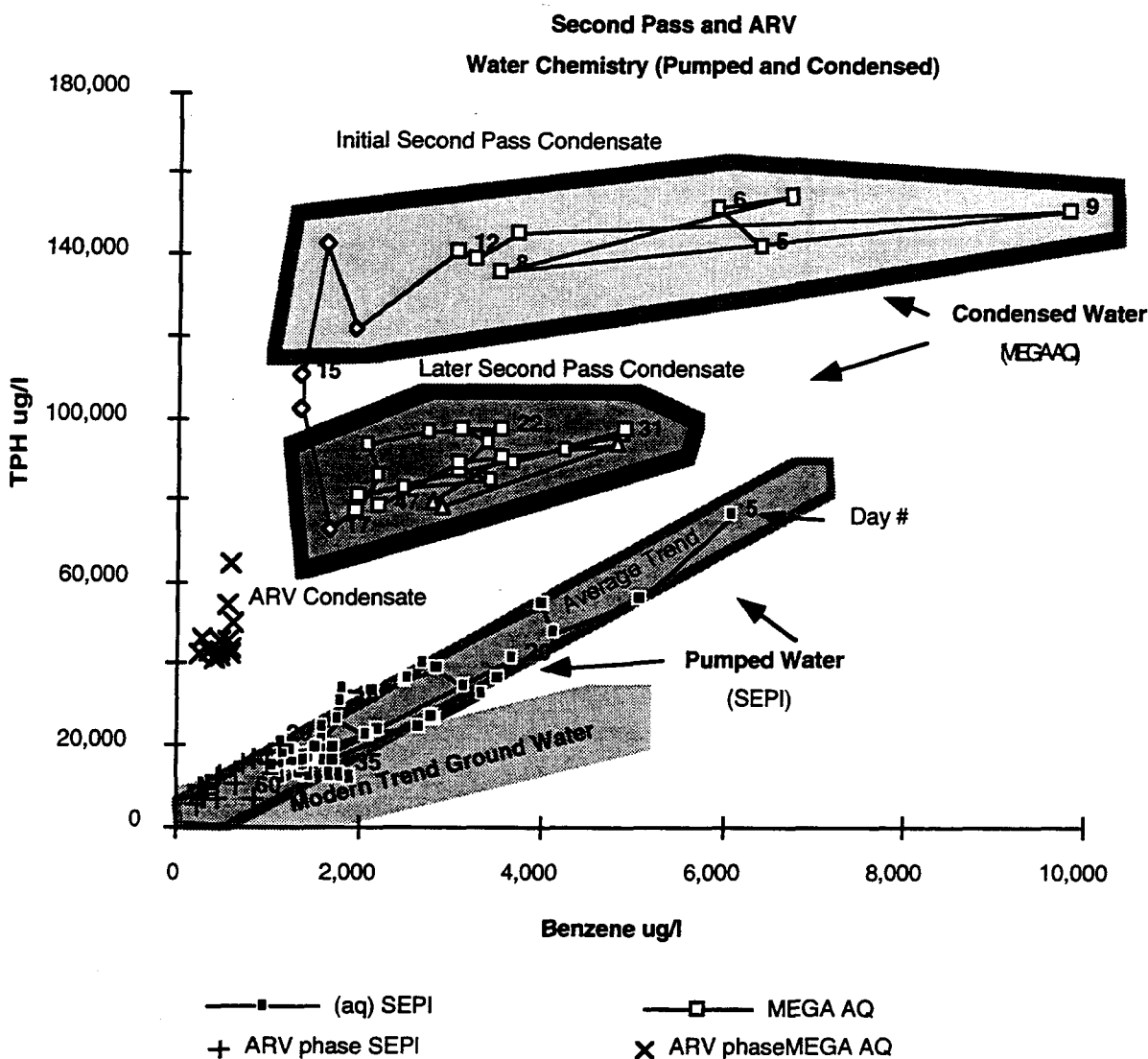


Figure 19. Aqueous analyses from the second pass and ARV. Sequential data points are connected for second pass data. The observed trend from Figure 18 is labeled "Modern Groundwater," Other fields are defined by the limits of this data.

(Figure 21). At this time, no Dynamic Underground Stripping extraction had taken place; gasoline had presumably been fractionated somewhat in the central spill area by the previous vacuum extraction experiment of Cook et al. (1991). Benzene concentrations were very high, corresponding to high TPH concentrations. The chemistry of water sampled in these wells still fell above the historical trend (Figure 17) but was much higher in benzene /TPH ratio and gasoline content than water extracted during Dynamic Underground Stripping, or than the soil gasoline chemistry. This appears to represent the mobilization and aqueous partitioning of soil gasoline without the separation of vapor and liquid that occurred in the Dynamic Underground Stripping extraction system. Benzene (and presumably other BTEX compounds) occur in greater abundance than in the soil chemistry because of their greater solubility in water. Groundwater temperatures did not increase significantly during this period over the entire pad, but near electrical injectors temperatures were quite elevated (at least the boiling point of water; Buettner, *this report*).

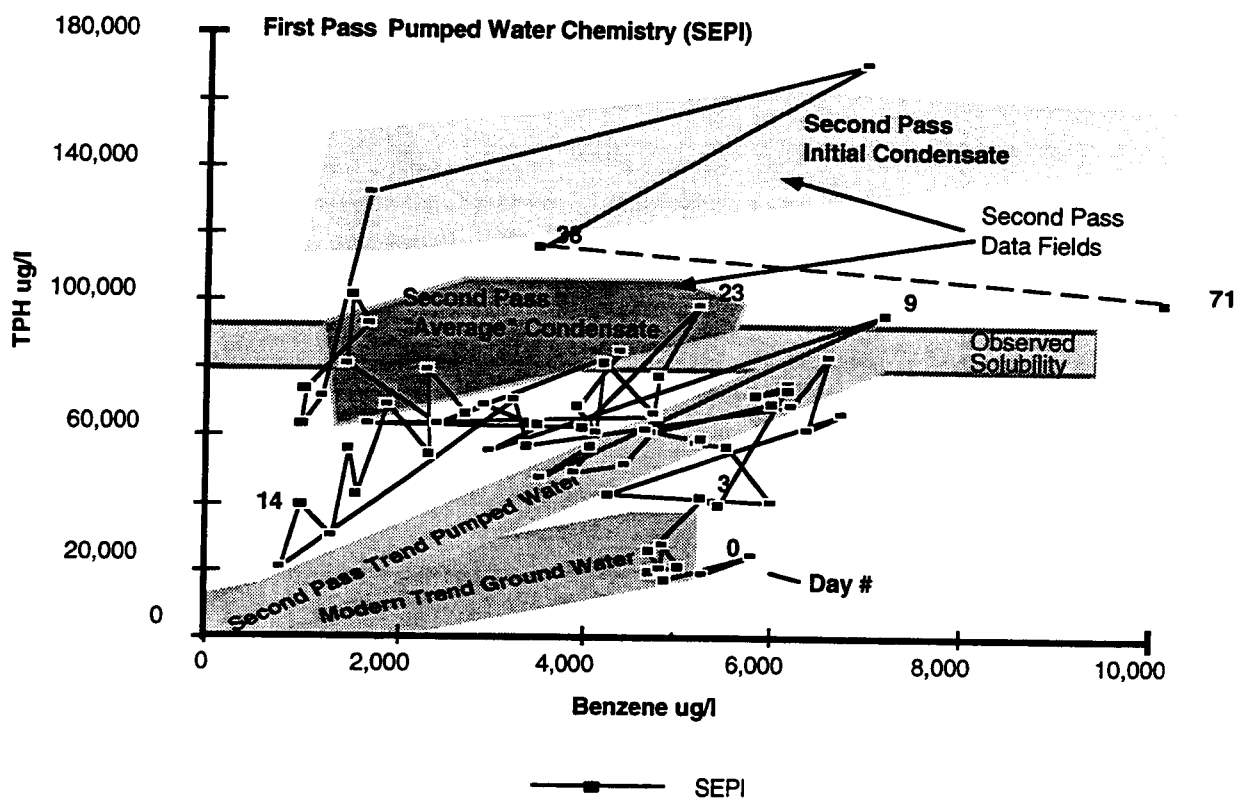


Figure 20. First-pass data compared to fields defined by modern groundwater data and second-pass pumped water and condensate.

Vapor generated during heat soak periods. One of the most remarkable chemical effects we observed was the generation during the “heat soak” between the first and second passes of a very TPH-rich, light-hydrocarbon-rich vapor phase, which was also quite soluble in water. The SEPI data at the close of the first pass may also reflect this vapor-phase formation.

This vapor was originally assumed to represent gasoline that had been “hidden” from the atmosphere since the spill, presumably by entrapment in tight soils. As such, it would have retained its original component of light (C4 and C5) hydrocarbons, which are normally rapidly lost from hydrocarbon spills (Lyman et al., 1991). However, this mechanism should also preserve benzene, which is less volatile. Bioremediation of benzene would not occur in a hypothetical area that is not in contact with the atmosphere because the process requires oxygen.

A more likely explanation is that this vapor represents the high-temperature equilibration (Henry’s Law partitioning) of gasoline liquid, water, and vapor. The BTEX compounds preferentially remain in the water, as seen in Figure 20, but the lighter hydrocarbons enter the vapor phase. C4 and C5 aliphatic compounds have very high Henry’s Law constants and very high free-product vapor pressures. Thus, any remaining C4 and C5 compounds appear to have equilibrated into the vapor phase during the heat soak period. This is probably the only “equilibrium” vapor extracted during the Dynamic Underground Stripping process. All the other vapor appears to represent volume-vaporization processes where most of

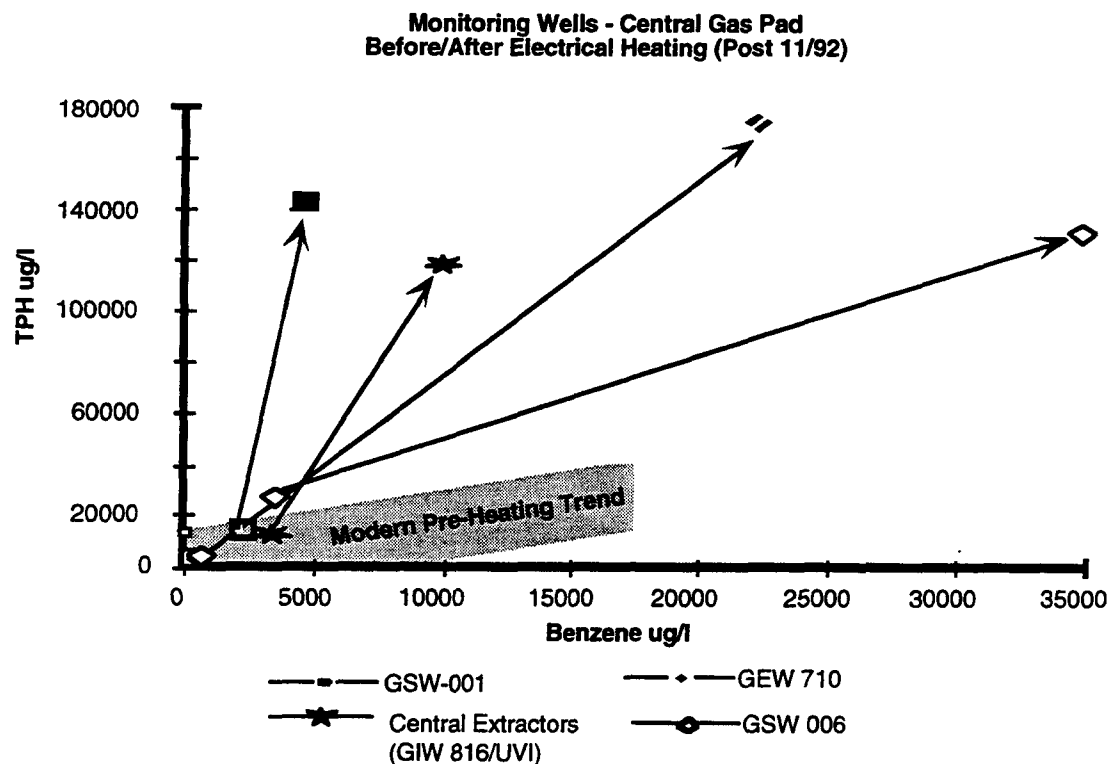


Figure 21. Groundwater analyses from central wells at the gasoline spill site before Dynamic Underground Stripping, and after the electric preheat phase (Buettner, *this report*). Note the increased benzene range relative to Figures 14-17.

the liquid in a volume is converted to vapor and removed. Some fractionation occurred; the overall TPH/benzene composition of extracted water moved slowly toward the soil TPH/benzene ratio as benzene was removed. The vapor removed during the ARV phase was slightly more TPH-rich than the original soil due to preferential extraction of benzene during the earlier passes.

Chemistry of Recovered Liquid Hydrocarbon. Much of the gasoline removed was in the form of liquid that was recycled (see below). Accurate chemical measurements were not made on much of this material. During the second pass and ARV phase, the gasoline recovered in the condensate oil-water separator (MEGA HC) was analyzed for the ten most abundant hydrocarbons. Jovanovich (*this report*) shows that the composition became progressively heavier and less volatile as the extraction continued (Figure 22). This is consistent with the results of the MEGA AQ analyses. Unfortunately, benzene was a small component of the recovered gasoline and was not measured separately, and we cannot compare its concentration to these results.

MEGA HC Gasoline Composition Second Pass and ARV: 10 Largest Components

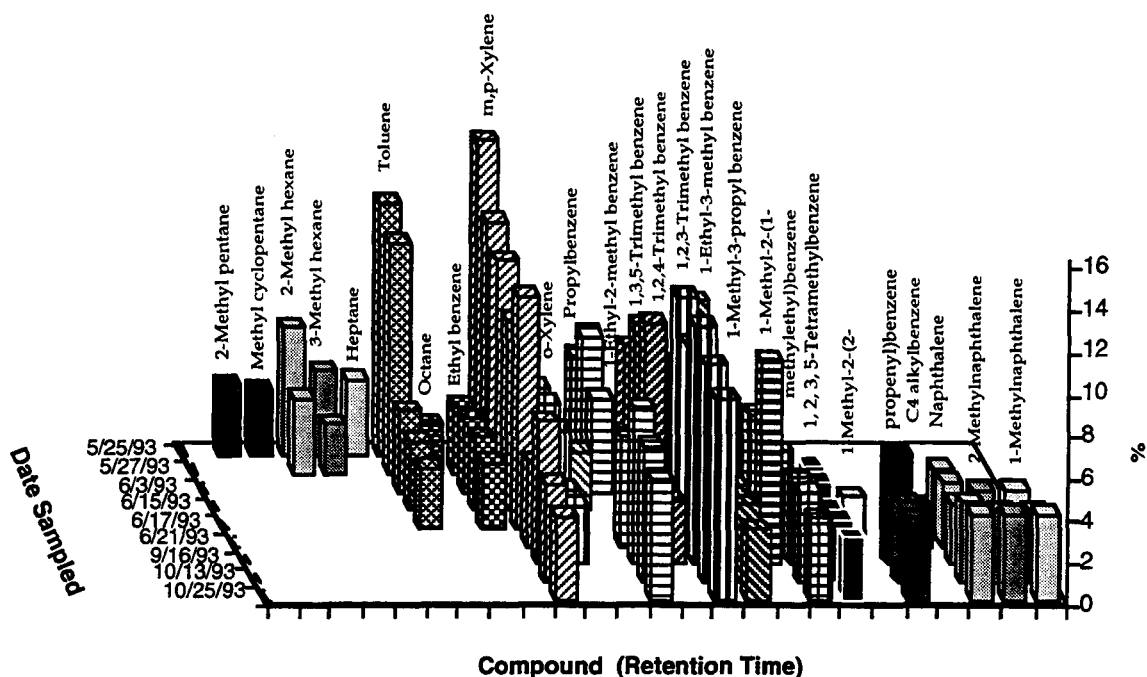


Figure 22. Composition of gasoline recovered from the condensate oil-water separator (MEGA HC) during the second pass and ARV phase. Only the top ten compounds are reported for each analysis; identifications are approximate based on retention time and mass (1-amu resolution). Jovanovich, (*this report*), Sweeney et al., (*this report*).

Conclusions

The total approximate errors in each of the mass balance measurements were given in the preceding sections and are summarized in Table 6.

Table 6. Approximate errors associated with the gasoline volume estimates.

<i>Gallons Gasoline</i>	Vapor	Condensate	Water	Pass Totals
First Pass	1260 (± 20)	260 + 100 – 10	159 \pm 20	1680 + 140 – 50
Second Pass	3805 \pm 600	1012 \pm 25	106 \pm 15	4923 \pm 640
ARV	909 \pm 150	107 \pm 5	59 \pm 7	1075 \pm 162
Stream Totals	5974 \pm 770	1379 + 130 – 40	324 \pm 42	
Grand Total				7680 + 950 – 850

Tables 7, 8, and 9 show the daily total gasoline recovery rate for each of the streams during each of the three phases of Dynamic Underground Stripping. These are the data used for the total volume calculations. In addition to this measured gasoline, other removal mechanisms have been active. Bioremediation has removed a significant, but as yet unquantified, amount (Krauter, *this report*). Venting to the surface, especially near the center of the spill as evidenced in the GSB 015 data, has occurred.

Table 7. Mass balance, first pass.

Date	1st pass elapsed time	Oil/water separator Megator rate	Carbon trailer daily rate	Vapor: Calculated post-cond. conc. (from total liquid)	Vapor: Measured VESI BTEX	Total vapor gasoline IF 27.5% BTEX	Total vapor gasoline IF 50% BTEX	Groundwater SEPI dissolved hydrocarbons	Groundwater SEPI dissolved rate	Total gasoline removal rate
(Date)	(days)	(gal/day)	(gal/day)	(ppm "HC")	(ppmv)	(ppmv)	(ppmv)	(µg/L)	(gal/day)	(gal/day)
2/3/93	1									
2/4/93	2	0	18	732	421	1532	843	3	3	21
2/5/93	3	0	44	1789	353	1282	705	5	2	46
2/6/93	4	0	5	203	232	845	465	8	3	8
2/7/93	5	0	19	773	170	618	340	13	5	24
2/8/93	6	0	6	244	409	1486	818	22	9	15
2/9/93	7	0	36	1464	293	1065	586	33	11	47
2/10/93	8	0	24	976	252	918	505	36	3	27
2/11/93	9	0	27	1098	1096	3985	2192	39	3	30
2/12/93	10	0	20	813	1096	3985	2192	42	3	23
2/13/93	11	0	19	773	1096	3985	2192	46	4	23
2/14/93	12	75	43	1748	1940	7053	3879	50	4	122
2/15/93	13	0	83	3375	1389	5050	2777	55	5	88
2/16/93	14	40	31	1260	1003	3649	2007	57	2	73
2/17/93	15	0	47	1911	1003	3649	2007	59	2	49
2/18/93	16	0	49	1984	618	2248	1236	61	2	51
2/19/93	17	0	25	1016	356	1293	711	65	4	29
2/20/93	18	0	11	447	93	338	186	67	2	13
2/21/93	19	0	10	406	97	351	193	69	2	12
2/22/93	20	20	6	264	532	1934	1064	73	4	30
2/23/93	21	0	14	569	532	1934	1064	78	5	19
2/24/93	23	0	46	1870	532	1934	1064	88	10	56
2/25/93	24	0	8	325	532	1934	1064	88	0	8
2/26/93	25	0	28	1138	532	1934	1064	92	4	32
2/27/93	26	0	44	1788	532	1934	1064	98	6	50
2/28/93	27	0	45	1829	532	1934	1064	103	5	50
3/1/93	28	0	42	1727	532	1934	1064	108	5	47
3/2/93	29	0	47	1910	532	1934	1064	113	5	52
3/3/93	30	0	38	1544	532	1934	1064	117	4	42
3/4/93	31	0	46	1870	532	1934	1064	121	4	50
3/5/93	32	0	50	2052	532	1934	1064	125	4	54
3/6/93	33	0	49	1991	532	1934	1064	128	3	52
3/7/93	34	0	43	1748	532	1934	1064	130	2	45
3/8/93	35	50	24	975	532	1934	1064	134	4	78
3/9/93	36	35	36	1463	532	1934	1064	139	5	76
3/10/93	37	0	21	853	967	3516	1934	139	4	25
3/11/93	38	0	34	1382	967	3516	1934	139	4	38
3/12/93	39	0	37	1504	967	3516	1934	139	4	41
3/13/93	40	40	46	1870	967	3516	1934	139	4	90
3/14/93	41	0	42	1727	967	3516	1934	139	4	46

Totals

260

1264

Gallons

159

1683

Liters

6373

Kilograms @ 737 g/L

4697

Pounds

12583

Table 8. Mass balance, second pass.

Date	Elapsed time (days)	Total vapor L	Total hc average mg/L	Burned IC engine from ppm mg/L data gal	Corrected (averaged) condensed liquid gasoline gal	Total vapor stream gal	SEPI conc. mg/L	Daily pumped total gal	Gasoline in liquid stream gal	Daily total all streams gal	Running total all gal
5/24/93	1	1,091,523	253	99	0	99	85		0.0	99.0	99
5/25/93	2	1,492,334	238	127	41	168	85		0.0	168.3	267
5/26/93	3	2,271,676	130	106	61	167	85		0.0	166.9	434
5/27/93	4	3,203,920	112	129	38	167	85		0.0	166.6	601
5/28/93	5	4,486,674	52	84	55	139	77		0.0	138.6	739
5/29/93	6	4,886,633	39	68	51	119	56	61940	4.7	124.0	863
5/30/93	7	5,512,571	87	172	50	222	48	70955	4.6	226.4	1090
5/31/93	8	5,978,888	104	223	44	267	55	70000	5.2	271.7	1362
6/1/93	9	6,236,944	50	112	33	145	40	63770	3.5	148.0	1510
6/2/93	10	6,074,354	55	120	33	153	36	71400	3.5	156.0	1666
6/3/93	11	6,660,110	46	110	30	140	33	63150	2.8	142.6	1808
6/4/93	12	6,698,863	27	65	31	96	33	71520	3.2	99.4	1908
6/5/93	13	6,577,432	27	64	35	99	34	88940	4.1	103.2	2011
6/6/93	14	6,149,289	32	71	19	90	31	77030	3.2	92.8	2104
6/7/93	15	6,139,250	24	53	16	69	24	71500	2.4	71.5	2175
6/8/93	16	5,925,849	35	74	11	85	36	76360	3.8	89.1	2264
6/9/93	17	5,398,566	38	74	11	85	39	74810	3.9	88.5	2353
6/10/93	18	5,079,951	43	78	11	89	34	73950	3.4	92.7	2446
6/11/93	19	5,082,617	37	67	21	88	36	78460	3.8	92.2	2538
6/12/93	20	5,040,256	36	65	21	86	41	70940	4.0	90.0	2628
6/13/93	21	5,054,628	46	83	34	117	12	66650	1.1	118.2	2746
6/14/93	22	5,349,177	51	98	32	130	32	66360	2.9	132.7	2879
6/15/93	23	5,238,084	55	103	17	120	26	69230	2.4	122.7	3001
6/16/93	24	5,050,226	52	94	11	105	24	77210	2.6	107.7	3109
6/17/93	25	4,437,041	48	76	3	79	23	77340	2.4	81.4	3191
6/18/93	26	5,395,381	38	73	3	76	22	75670	2.3	78.4	3269
6/19/93	27	4,695,380	27	45	3	48	26	72510	2.6	50.6	3320
6/20/93	28	5,061,231	18	33	25	58	21	78110	2.2	60.2	3380
6/21/93	29	5,061,231	21	38	28	66	16	81100	1.8	68.2	3448
6/22/93	30	5,098,878	46	84	16	100	16	80050	1.7	101.8	3550
6/23/93	31	5,006,539	52	93	22	115	17.9	70,210	1.7	116.7	3667
6/24/93	32	4,956,712	50	89	20	109	16	80,080	1.7	110.9	3778
6/25/93	33	5,096,552	51	93	5	99	15.7	86,900	1.9	100.5	3878
6/26/93	34	5,196,975	45	84	5	89	12.7	85,290	1.5	90.8	3969
6/27/93	35	5,196,975	26	48	5	54	12.1	85,440	1.4	55.3	4024
6/28/93	36	5,107,624	28	51	15	66	13	82,810	1.5	67.8	4092
6/29/93	37	5,089,617	27	49	23	72	12.4	83,870	1.4	73.7	4166
6/30/93	38	5,195,913	13	24	26	50	13.2	85,670	1.5	51.7	4217
7/1/93	39	5,139,923	17	31	27	58	15.5	87,440	1.8	59.7	4277
7/2/93	40	5,280,739	47	89	25	114	19	84,670	2.2	116.0	4393
7/3/93	41	5,217,597	45	84	11	95	15.9	83,790	1.8	97.0	4490
7/4/93	42	5,155,428	39	72	10	82	15.5	81,560	1.7	84.2	4574
7/5/93	43	5,461,273	43	84	8	92	14.4	80,100	1.6	93.5	4668
7/6/93	44	5,260,421	40	75	8	83	15.6	77,990	1.7	84.9	4753
7/7/93	45	5,421,017	36	70	7	76	16.2	78,290	1.7	78.2	4831
7/8/93	46	5,526,531	29	57	6	63	16.9	67,410	1.5	64.8	4896
7/9/93	47	1,903,210	31	21	5	26	15.9	85,920	1.9	28.2	4924
Totals		235,642,006		3805	1012	4817		3,216,395	107		4924
											Gallons 4924
											Liters 18639
											Kilograms @ 737 g/L 13737
											Pounds 36805

Table 9. Mass balance, ARV (Sweeney et al., this report).

Date	Elapsed time (days)	Daily extracted vapor volume (scfd)	HC conc. in vapor (ppmv)	Burned gasoline rate (ICE) (gal/day)	Daily condensed gasoline (gal/day)	Total vapor stream (gal/day)	SEPI HC conc. in water mg/L	Daily vol. of water pumped (gal/day)	Daily aqueous gasoline removal (gal/day)	Daily combined gasoline removal (gal)	Cumul. combined gasoline removal (gal)
10/4	1	93,000	5,200	18.2	0.0	18		42,400		18.2	18
10/5	2	176,000	6,000	40.1	12.3	52	7,400	81,200	0.8	53.1	71
10/6	3	168,000	5,900	37.7	6.8	44	13,800	74,200	1.4	45.8	117
10/7	4	120,000	5,630	25.6	4.1	30	20,300	70,100	1.9	31.6	149
10/8	5	159,000	3,790	22.8	6.8	30	19,300	69,600	1.8	31.4	182
10/9	6	158,000	3,900	23.3	6.1	29	18,300	69,200	1.7	31.1	213
10/10	7	160,000	3,400	20.6	2.7	23	17,300	67,600	1.5	24.8	237
10/11	8	168,000	3,000	19.1	1.4	20	16,300	67,400	1.5	21.9	260
10/12	9	165,000	3,307	20.7	1.4	22	16,200	66,300	1.4	23.5	284
10/13	10	159,000	3,400	20.4	1.4	22	16,000	66,200	1.4	23.2	307
10/14	11	160,000	2,920	17.7	1.4	19	15,900	66,100	1.4	20.5	327
10/15	12	162,000	2,920	17.9	4.1	22	15,900	67,000	1.4	23.4	351
10/16	13	155,000	2,910	17.1	0.0	17	15,900	66,900	1.4	18.5	369
10/17	14	160,000	2,340	14.1	2.7	17	15,800	66,700	1.4	18.3	387
10/18	15	156,000	3,970	23.5	1.4	25	15,800	67,600	1.4	26.3	414
10/19	16	160,000	4,260	25.8	0.0	26	15,200	66,900	1.3	27.2	441
10/20	17	166,000	3,520	22.2	6.8	29	14,600	67,100	1.3	30.3	471
10/21	18	168,000	3,970	25.2	0.7	26	13,900	67,300	1.2	27.1	498
10/22	19	173,000	3,818	25.0	0.0	25	13,300	65,000	1.1	26.1	524
10/23	20	144,000	3,583	19.5	0.0	20	11,500	55,100	0.8	20.4	545
10/24	21	130,000	3,170	15.5	0.0	16	9,700	47,700	0.6	16.2	561
10/25	22	178,000	3,090	20.8	0.0	21	7,900	64,700	0.7	21.5	582
10/26	23	124,000	6,660	31.2	0.7	32	8,200	64,100	0.7	32.6	615
10/27	24	100,000	6,440	24.5	0.0	24	8,500	65,000	0.7	25.2	640
10/28	25	101,000	2,810	10.7	0.0	11	8,800	61,700	0.7	11.4	652
10/29	26	116,000	6,240	27.4	1.4	29	9,100	63,100	0.8	29.5	681
10/30	27	140,000	6,140	32.5	1.4	34	8,500	64,900	0.7	34.6	716
10/31	28	139,000	5,660	29.9	0.0	30	7,900	61,300	0.6	30.5	746
11/1	29	107,000	5,880	23.8	13.6	37	7,300	49,100	0.5	37.9	784
11/2	30	114,000	6,870	21.1	2.7	24	7,300	65,200	0.6	23.8	808
11/3	31	123,000	2,500	11.6	0.0	12	7,300	74,600	0.7	11.6	820
11/4	32	116,000	1,880	8.2	0.0	8	7,300	72,000	0.7	8.2	829
11/5	33	65,000	37	0.1	0.0	0	7,300	39,300	0.4	0.0	830
11/6	34	000	0	0.0	0.0	0		0	0.0	0.0	830
11/7	35	000	0	0.0	0.0	0		0	0.0	0.0	830
11/8	36	63,000	178	0.4	0.0	0	5,400	45,200	0.3	0.0	831
11/9	37	140,000	926	4.8	0.0	5	5,400	81,400	0.6	4.9	836
11/10	38	144,000	993	5.3	0.0	5	5,400	76,300	0.5	5.4	842
11/11	39	153,000	1,870	10.6	0.3	11	7,500	71,400	0.7	11.7	858
11/12	40	151,000	39	0.2	0.0	0	7,500	72,600	0.7	0.9	859
11/13	41	145,000	1,670	9.0	0.0	9	7,500	69,900	0.7	9.7	869
11/14	42	142,000	1,470	7.8	0.0	8	7,500	71,000	0.7	8.5	877
11/15	43	118,000	235	1.0	0.0	1	11,100	65,700	1.0	2.0	879
11/16	44	146,000	240	1.3	0.0	1	11,100	71,500	1.0	2.3	881
11/17	45	124,000	310	1.4	0.0	1	11,100	57,600	0.8	2.3	884
11/18	46	86,000	310	1.0	0.0	1	12,500	72,300	1.2	2.2	886
11/19	47	51,000	310	0.6	12.3	13	12,500	59,700	1.0	13.8	902
11/20	48	58,000	2,930	6.4	3.4	10	12,500	70,300	1.1	10.9	914
11/21	49	61,000	3,490	6.6	1.4	8	12,500	70,300	1.1	9.1	923
11/22	50	81,000	1,800	8.8	1.4	10	10,000	69,000	0.9	11.1	934
11/23	51	70,000	2,760	7.7	2.7	10	10,000	68,900	0.9	11.3	947
11/24	52	61,000	3,000	6.7	0.0	7	10,000	30,600	0.4	7.1	954
11/25	53	000	0	0.0	0.0	0	10,000	0	0.0	0.0	954
11/26	54	000	0	0.0	0.0	0	10,000	0	0.0	0.0	954
11/27	55	000	0	0.0	0.0	0	10,000	0	0.0	0.0	954
11/28	56	000	0	0.0	0.0	0	10,000	0	0.0	0.0	954
11/29	57	46,000	3,320	5.6	0.0	6	10,800	102,400	1.4	7.1	961
11/30	58	161,000	1,220	7.3	1.4	9	10,800	68,600	1.0	9.7	970
12/1	59	158,000	1,460	8.6	0.0	9	10,800	77,800	1.1	9.7	980
12/2	60	150,000	1,620	9.1	0.0	9	10,800	70,900	1.0	10.1	990
12/3	61	146,000	1,510	8.2	0.0	8	8,700	69,000	0.8	9.0	999
12/4	62	153,000	1,510	8.6	0.0	9	8,700	71,600	0.8	9.4	1009
12/5	63	149,000	1,570	8.4	0.0	8	8,700	70,700	0.8	9.2	1018
12/6	64	153,000	2,010	11.5	0.0	11	10,300	67,900	0.9	12.4	1030
12/7	65	161,000	1,870	11.2	0.0	11	10,300	71,500	1.0	12.2	1042
12/8	66	153,000	1,770	10.1	0.0	10	10,300	68,300	0.9	11.0	1053
12/9	67	104,000	1,440	5.6	1.4	7	10,400	24,900	0.3	7.3	1061
12/10	68	154,000	1,000	5.8	0.0	6	10,400	5,100	0.1	5.8	1066
12/11	69	163,000	1,010	6.2	2.7	9	10,400	13,600	0.2	9.1	1076
12/12	70	158,000	1,150	6.8	0.0	7	10,400	300	0.0	6.8	1082
12/13	71	59,000	1,110	2.5	0.0	3	10,400	0	0.0	2.5	1085
Totals		8,545,000		909	107	1,016		4,028,900	59	Gallons Liters Kilograms Pounds	1085 4107 3027 8109

Finally, some gasoline may have undergone chemical oxidation during either the electrical heating or steam phases. Ignition of the gasoline under these circumstances is limited by the lack of oxygen (the ground acts as a flame arrester) (Siegel, *this report*) but some gasoline would presumably have been oxidized by the oxygen present in the soil.

The overall chemical trends observed during the experiment indicate that Dynamic Underground Stripping effectively removes contamination from soil and groundwater via a mass-removal mechanism where fractionation is not a major process (or is subsumed by the cyclic nature of Dynamic Underground Stripping). In the LLNL test, most of the gasoline was removed in the vapor stream, but little condensation of gasoline occurred in the surface treatment system. The steam extracted from the formation condensed and equilibrated with pumped groundwater within the extraction wells. Large volumes of extracted inert gas (presumably air) carried much of the gasoline into the IC engines, and relatively little was condensed.

References

- Lyman, W.J., Reidy, P.J., Levy, B. (1991), "Assessing UST corrective action technology," *A scientific evaluation of the mobility and degradability of organic contaminants in the subsurface environments*, U.S. EPA Report, EPA/600/2-91/053 (September, 1991).
- Cook, G.E., Oberdorfer, J.A., and Orloff, S P. (1991), *Remediation of a gasoline spill by vapor extraction*, Lawrence Livermore National Laboratory, Livermore, CA, Lawrence Livermore National Laboratory, UCRL-JC-108064.
- Dresen, M.D., Hoffman, F., and Lovejoy, S. (1986), *Subsurface distribution of hydrocarbons in the building 403 area at LLNL*, Lawrence Livermore National Laboratory, UCID-20787.
- Nichols, E.M., Dresen, M.D., and Field, J.E., (1988), *Proposal for pilot study at LLNL building 403 gasoline station area*, Lawrence Livermore National Laboratory, UCAR-10248.

